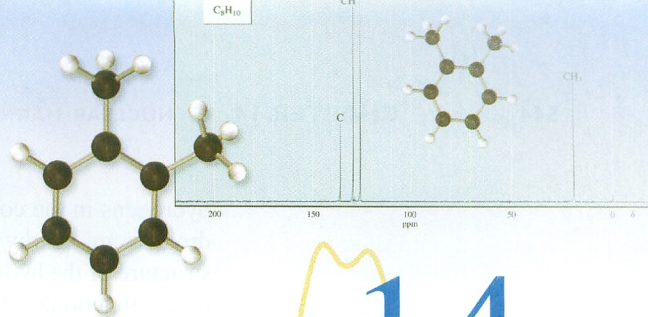


# Nuclear Magnetic Resonance Spectroscopy



## CHAPTER

# 14

AS WE SAW IN CHAPTER 13, infrared (IR) spectroscopy can be used to determine which functional group is present in a compound. This chapter discusses proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy. These techniques complement IR spectroscopy because they provide information about the hydrocarbon part of the molecule. The combination of IR and NMR spectroscopy often provides enough data to determine the structure of an unknown compound.

Proton magnetic spectroscopy is discussed first. After a brief discussion of the theory behind this technique, the use of  $^1\text{H}$ -NMR spectroscopy to determine the structure of the hydrocarbon part of the compound is described. Next the use of  $^{13}\text{C}$ -NMR spectroscopy to gain information about the carbons in the compounds is presented. Finally, examples of the use of various combinations of these techniques to identify unknown organic compounds are discussed.

## 14.1 PROTON MAGNETIC RESONANCE SPECTROSCOPY

The nuclei of certain isotopes of some elements have two (or more) energy states available when they are in a magnetic field. The transitions between these energy states can be investigated by using the technique of NMR spectroscopy. Although many nuclei exhibit this phenomenon, the two that are of most use to organic chemists are the hydrogen nucleus (a proton,  $^1\text{H}$ ) and the nucleus of the isotope of carbon with an atomic mass number of 13 ( $^{13}\text{C}$ ).

Proton magnetic resonance spectroscopy provides information about the relative numbers of different kinds of

### MASTERING ORGANIC CHEMISTRY

- ▶ Predicting the Chemical Shifts, Multiplicity, and Integrals of Peaks in the  $^1\text{H}$ -NMR Spectrum of a Compound
- ▶ Predicting the Number of Peaks and Their Chemical Shifts in the  $^{13}\text{C}$ -NMR Spectrum of a Compound
- ▶ Determining the Hydrocarbon Skeleton of a Compound by Examination of Its  $^1\text{H}$ -NMR and/or  $^{13}\text{C}$ -NMR Spectrum
- ▶ Determining the Structure of a Compound Using IR and NMR Spectroscopy

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hydrogens in the compound, the nature of the carbons bonded to them, and which hydrogens are nearby. From this information it is possible to get a good idea about the structure of the hydrocarbon part of the compound. In combination with the knowledge of the functional group obtained from the IR spectrum, the NMR spectrum often enables the structure of a compound to be assigned with certainty.

Before we look at the theory behind the NMR technique, let's look at a sample spectrum to find out what kind of information it provides. Figure 14.1 shows the  $^1\text{H}$ -NMR spectrum of 3-pentanone. Note that the absorption peaks extend up from the baseline at the bottom of the spectrum, in contrast to IR spectra.

Three types of information are present in a NMR spectrum:

1. The position on the  $x$ -axis. Called the **chemical shift**, this provides information about the carbon (or other atom) to which the hydrogen is attached.
2. The number of peaks in each group. Called the **multiplicity**, this provides information about the other hydrogens that are near the hydrogen or hydrogens that produce the peaks.
3. The **integral**. The area under a group of peaks is proportional to the number of hydrogens that produce that group of peaks.

Many NMR spectrometers provide the integral in the form of a line drawn on the spectrum that increases in height in proportion to the total area of the peaks. The height of each "step" is proportional to the number of hydrogens that produce the peaks under

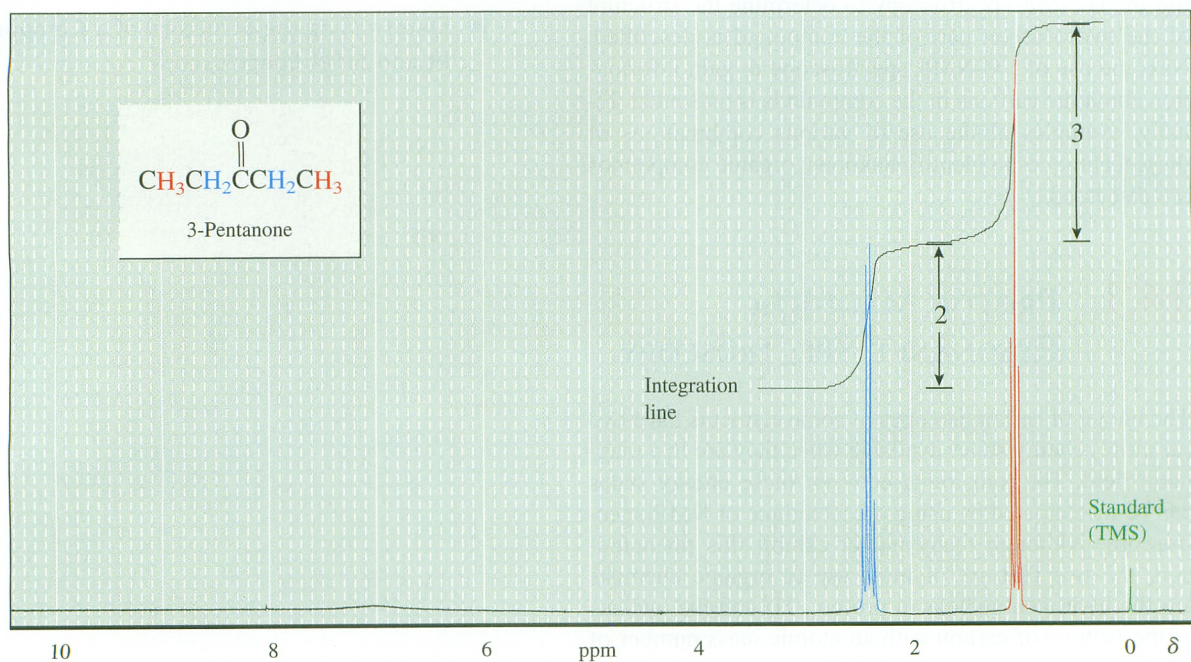


Figure 14.1

THE  $^1\text{H}$ -NMR SPECTRUM OF 3-PENTANONE.



that step. The heights must be put into small whole number ratios to provide the relative numbers of each type of hydrogen. To simplify interpretation, the spectra in this book have already been integrated, and the relative numbers of hydrogens for each group of peaks are provided. However, remember that the actual numbers of hydrogens can be multiples of the numbers provided by the integrals.

## 14.2 THEORY OF $^1\text{H}$ -NMR

The following discussion of the theory behind  $^1\text{H}$ -NMR is adequate for our needs. The charge of some nuclei, including  $^1\text{H}$ , “spins” on the nuclear axis. This spinning charge generates a small magnetic field. For the purposes of further discussion, the nucleus can be considered as a small bar magnet.

The hydrogen nucleus has two possible spin states that have identical energies under normal circumstances. However, if the atoms are placed in an external magnetic field—that is, between the poles of a large magnet in the laboratory—then the spin states have different energies. As shown in Figure 14.2, one state has its magnetic field oriented in the same direction as the external magnetic field,  $B_0$ , and is lower in energy than the other state that has its field oriented in opposition to the external field. With two states of different energy, spectroscopy can be done.

The difference in energy between the two states is related to the strength of the external magnetic field by the equation

$$\Delta E = h\gamma B_0/2\pi$$

where  $B_0$  is the strength of the external magnetic field and  $\gamma$  is the magnetogyric ratio, which differs for each kind of atomic nucleus.

The magnetogyric ratio is extremely small. Therefore,  $\Delta E$  is very small even when very large magnets are used. For example, early NMR spectrometers employed a 14,000-gauss (or 1.4-tesla) magnet. (The magnetic field of the Earth is about 0.5 gauss, whereas small magnets, such as those used to hold notes on a refrigerator, have fields

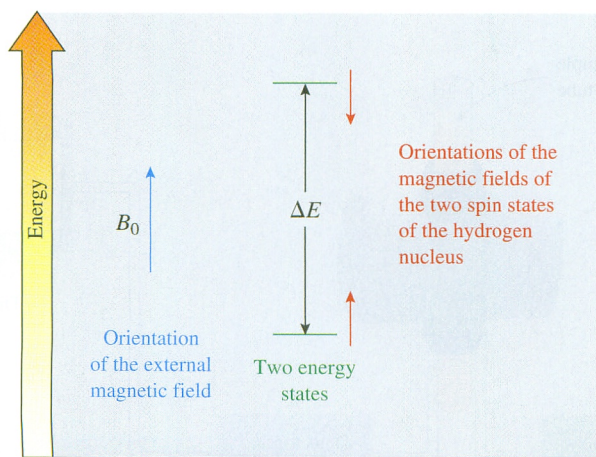


Figure 14.2

ENERGY LEVEL DIAGRAM FOR THE TWO SPIN STATES OF A HYDROGEN NUCLEUS IN A MAGNETIC FIELD.



of hundreds of gauss.) For these instruments,  $\Delta E$  is about  $10^{-6}$  kcal/mol, requiring radiation with a frequency of  $60 \times 10^6 \text{ s}^{-1}$  or 60 MHz. Because the two energy states differ by such a small amount of energy, the number of nuclei with the lower energy is only slightly larger than the number with the higher energy.

Better spectra are obtained with larger  $\Delta E$ 's, which require stronger magnetic fields. Therefore, many current NMR instruments use superconducting magnets, cooled with liquid helium, with fields that are substantially greater than 1.4 tesla. Instruments that operate at 200 MHz (4.67-tesla magnet) and 400 MHz (9.33-tesla magnet) are relatively common, and some with even larger magnets, although expensive, are also available. The spectra in this book were obtained on instruments operating at 200 or 400 MHz.

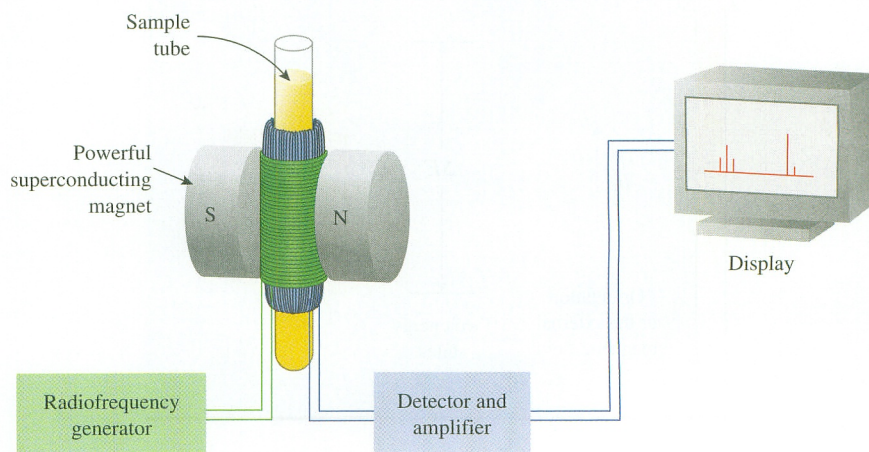
Other nuclei, such as  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^2\text{H}$ , and  $^{31}\text{P}$ , also have nuclear spins and can be studied with NMR techniques. However, because  $\gamma$  is different for these nuclei, they appear in a very different region of the spectrum from hydrogen and are not seen in a  $^1\text{H}$ -NMR spectrum. Both  $^{12}\text{C}$  and  $^{16}\text{O}$ , which are very common in organic compounds, do not have nuclear spin and therefore have no NMR absorptions.

Figure 14.3 shows a schematic diagram of a NMR spectrometer. The sample is dissolved in a suitable solvent and placed in a thin glass tube. The tube is placed between the poles of a powerful magnet. In the original type of instrument, the frequency of the electromagnetic radiation in the radio region is held constant and the strength of the magnetic field is slowly varied. When the magnetic field strength is such that the difference between the energy states of the hydrogen nucleus matches the energy of the radiation, the hydrogen absorbs the energy of the radiation and is said to be in resonance. It takes several minutes to scan the entire spectrum. Because of the time it takes to obtain a spectrum, this type of instrument is seldom used today.

In a modern NMR instrument, the magnetic field is held constant and the sample is irradiated with a brief pulse of radio-frequency irradiation. All the nuclei are excited simultaneously. As the nuclei return to their equilibrium population, a complex signal is generated. A computer converts this signal to a normal spectrum using a mathematical treatment called a Fourier transformation (FT). The advantage of an FT-NMR is that a spectrum can be obtained within a few seconds. This allows signal averaging to be used to increase the quality of the spectrum. In signal averaging, many spectra are summed by the computer. Because noise in each spectrum is random, it tends to cancel, whereas

**Figure 14.3**

**A SCHEMATIC DIAGRAM  
OF A NMR  
SPECTROMETER.**



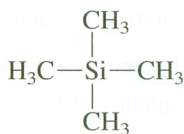


the signals of the nuclei get stronger as the spectra are added. In this way it is possible to get a good spectrum with a very small amount of compound in a relatively short period of time.

If all of the hydrogen nuclei in a compound absorbed at identical magnetic field strengths, the NMR technique would not be very useful. However, the exact field required for resonance depends on the local environment around the hydrogen. The electrons in the molecule circulate and create magnetic fields that oppose the external magnetic field. Therefore, the magnetic fields due to the electrons partially screen the hydrogen from the external magnetic field. Because the electron density varies throughout a molecule, different hydrogens require different field strengths to absorb the fixed frequency radiation. The variation is quite small, about 2500 Hz on an instrument that operates at 200 MHz, or about 0.001%, so a NMR spectrum must be obtained at very high resolution to be able to detect these differences.

## 14.3 THE CHEMICAL SHIFT

As discussed earlier, the chemical shift of a hydrogen signal—that is, the field required for the hydrogen to be in resonance—varies slightly with the chemical environment of the hydrogen. To measure chemical shifts, a small amount of a reference compound, usually tetramethylsilane (TMS), is added to the sample. The separation, in hertz, between the peak of interest and the peak due to TMS is measured. TMS is chosen as the reference because it has only one NMR peak and this peak occurs in a region of the spectrum where it does not usually overlap with other absorptions. Figure 14.4 illustrates the use of TMS as a reference compound in the spectrum of acetone.



Tetramethylsilane (TMS)

In the plot of a typical NMR spectrum, the field strength increases from left to right. The protons of TMS absorb at higher field than most other protons, so the TMS signal occurs at the right edge of the spectrum, as can be seen in Figure 14.4. The signals for most other types of hydrogens appear to the left of the TMS peak. Left on a NMR spectrum is termed the **downfield** direction; right is termed the **upfield** direction. The absorption for acetone occurs 436 Hz downfield from TMS in this spectrum.

Recall that the energy separation of the two nuclear spin states of the hydrogen is directly proportional to the magnetic field strength,  $B_0$ , of the NMR instrument. This means that the chemical shift, in hertz, also is directly proportional to the magnetic field strength. On an instrument with a 4.67-T magnet, which operates at a frequency of 200 MHz, the peak for acetone occurs 436 Hz downfield from TMS. On a spectrometer with a magnet that is twice as strong, which operates at a frequency of 400 MHz, the peak for acetone occurs 872 Hz downfield from TMS, farther downfield by a factor of 2. Chemical shifts that do not depend on the particular instrument that is used to acquire the spectrum are obtained by dividing the chemical shift, in hertz, by the operating frequency of the instrument. The result is multiplied by  $10^6$  to get a number of a more con-



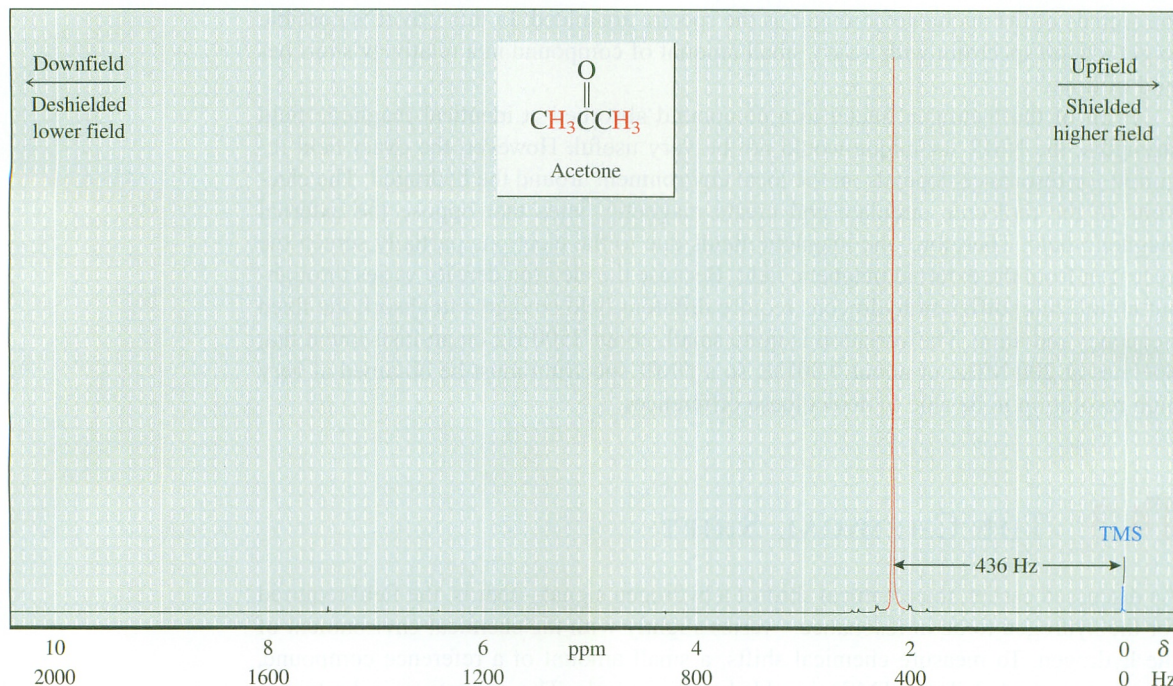


Figure 14.4

THE  $^1\text{H}$ -NMR SPECTRUM OF ACETONE AT 200 MHz.

venient magnitude. The resulting values for chemical shifts, called **parts per million** (ppm) or  $\delta$ , do not depend on the operating frequency of the instrument.

$$\delta = \frac{\text{Observed position of peak (Hz)}}{\text{Operating frequency of instrument (Hz)}} \times 10^6$$

The peak for acetone on a 200-MHz instrument occurs at 436 Hz, so the chemical shift is 2.18  $\delta$ :

$$\frac{(436 \text{ Hz})(10^6)}{(200 \times 10^6 \text{ Hz})} = 2.18 \delta$$

This peak also occurs at 2.18  $\delta$  on any other instrument, regardless of operating frequency. Figure 14.4 also shows  $\delta$  values.

#### PROBLEM 14.1

The absorption for the hydrogens of benzene appears 444 Hz downfield from TMS on an instrument that operates at 60 MHz.

- Calculate the position of this absorption in  $\delta$  units.
- Calculate the position of this absorption, in hertz, on 200- and 400-MHz instruments.
- What is the position of this absorption, in  $\delta$  units, on a 400-MHz instrument?

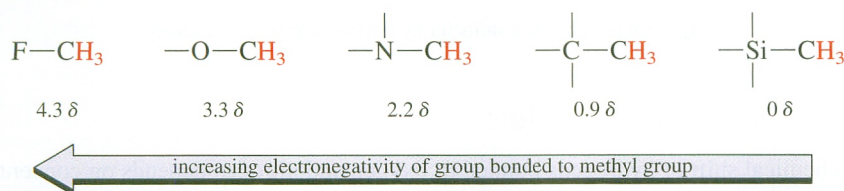
As discussed previously, the chemical shift of a hydrogen in a molecule is affected by the electrons surrounding it. The moving electrons generate their own small magnetic field that usually opposes the external magnetic field. The electrons shield the hy-



drogen from the external magnetic field, so the strength of the field experienced by the hydrogen is decreased. A hydrogen surrounded by a large amount of electron density requires a stronger external magnetic field to reach the resonance condition. Such a hydrogen is said to be shielded, and its absorption appears at a more upfield chemical shift (lower  $\delta$ ). Similarly, a hydrogen surrounded by a small amount of electron density is deshielded, and its absorption appears at a more downfield chemical shift (higher  $\delta$ ).

## Inductive Effects

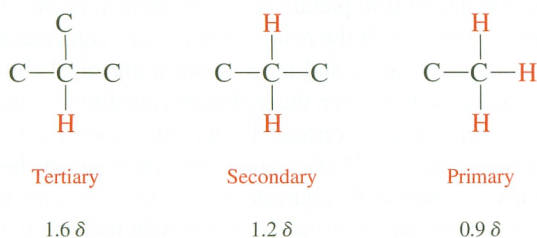
Consider a hydrogen bonded to a carbon. Its chemical shift depends on the other atoms bonded to that carbon. If these atoms are electronegative, they pull electron density away from the hydrogen and deshield it, resulting in absorption at higher  $\delta$ . Approximate chemical shifts of the hydrogens of methyl groups bonded to atoms of varying electronegativities are as follows:



Electronegative atoms deshield nearby hydrogens, resulting in a downfield shift.

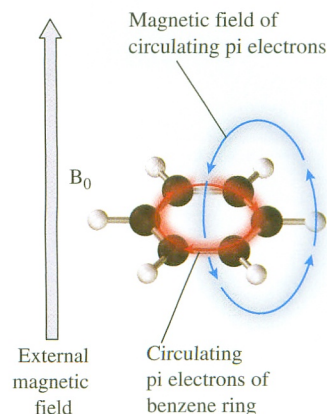
As the atom that is attached to the methyl group becomes more electronegative, the absorption for the hydrogen is shifted farther downfield. The peak for TMS occurs upfield from the peaks of most common organic compounds because silicon is less electronegative than most of the other elements encountered in organic compounds.

Carbon is slightly more electronegative than hydrogen. Thus, the absorption for hydrogens on a secondary carbon appears slightly downfield (approximately 0.3  $\delta$ ) from that for hydrogens on a primary carbon, and the peak for a hydrogen on a tertiary carbon appears even farther downfield (approximately 0.7  $\delta$  from the absorption for a primary hydrogen).



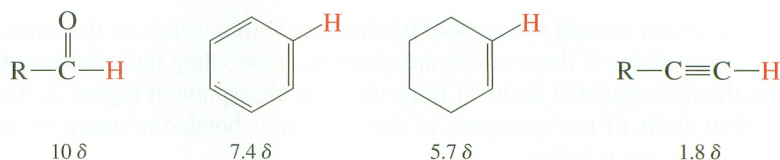
## Pi Electron Effects

Electrons in pi MOs circulate more readily in the external magnetic field than do those in sigma MOs because they are less strongly held by the nuclei. Depending on the exact geometry of the molecule, the magnetic field of these circulating electrons at the hydrogen of interest may be aligned with the external magnetic field, causing a downfield shift, or opposed to it, causing an upfield shift. This effect is especially pronounced in benzene derivatives, in which the magnetic field generated by the circulation of the electrons in the ring of conjugated orbitals opposes the external magnetic field in the center of the ring but is aligned with it around the periphery of the ring, where the hydrogen is located.





This “ring current effect” results in a large downfield shift for hydrogens attached to aromatic rings. The absorption for the hydrogens of benzene appears at  $7.4 \delta$ . A similar but smaller effect causes the hydrogens on the double bond of an alkene to appear downfield also. The absorptions for the vinyl hydrogens of cyclohexene appear at  $5.7 \delta$ . A hydrogen attached to the carbonyl carbon of an aldehyde appears even farther downfield, near  $10 \delta$ , owing to the additional inductive effect of the oxygen. Surprisingly, a hydrogen on carbon 1 of a terminal alkyne appears upfield, near  $1.8 \delta$ . In this case the field due to the circulating electrons opposes the external magnetic field at the hydrogen, causing an upfield shift.

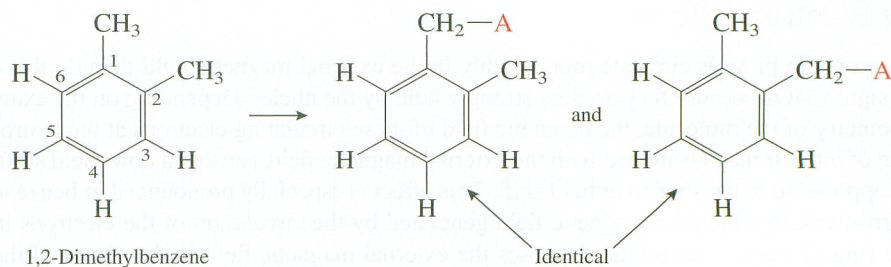


Approximate chemical shifts for hydrogens on pi bonded carbons

## Hydrogens Bonded to Heteroatoms

The chemical shift of hydrogens bonded to oxygen and nitrogen depends on concentration and temperature because the extent of hydrogen bonding varies with these factors. The peak for an alcohol usually occurs in the region of 2 to  $5 \delta$ , and the peak for an amine appears in the region of 1 to  $3 \delta$ . The peak for the hydrogen of a carboxylic acid, which forms dimers with strong hydrogen bonds, appears in the region of 10 to  $13 \delta$  and is quite characteristic.

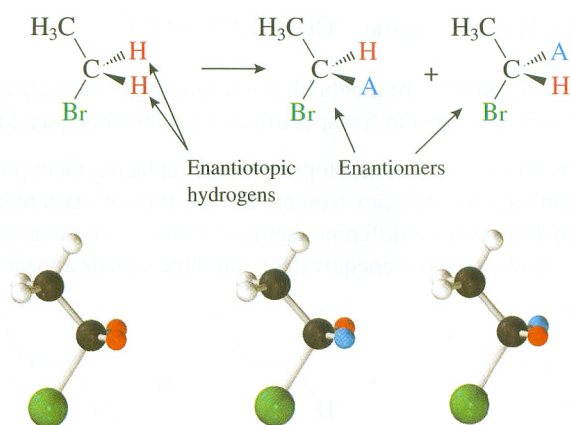
So far, the issue of how many signals occur in a  $^1\text{H}$ -NMR spectrum has not been directly addressed. Hydrogens have different chemical shifts (although coincidental overlaps do sometimes occur) unless they are chemically equivalent. *Chemically equivalent* means that the hydrogens would have identical chemical reactions. For example, it is readily apparent that all three hydrogens of a methyl group are chemically equivalent. However, for many compounds it may be less obvious which hydrogens are chemically equivalent. One way to make this determination is to picture replacing the hydrogens in question, one at a time, with an imaginary group, A. If the resulting imaginary compounds are identical, the hydrogens are chemically equivalent and have identical chemical shifts; if the resulting imaginary compounds are isomers, then the hydrogens are different and *may* result in different NMR signals. As an example, consider 1,2-dimethylbenzene. How many NMR signals are expected for this compound? Let's begin by determining whether the hydrogens on the two methyl groups are chemically equivalent. The two structures that result from replacing a hydrogen on one or the other methyl group with imaginary group A are identical, so the hydrogens of the methyl groups are chemically equivalent.



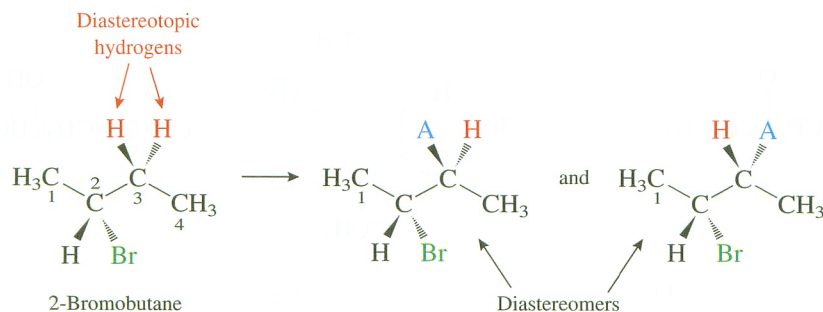


Similar transformations show that the two hydrogens on C-3 and C-6 are chemically equivalent, as are the two on C-4 and C-5. Therefore, three absorptions are expected in the NMR spectrum: one for all six methyl hydrogens, one for the two hydrogens on C-3 and C-6, and one for the two hydrogens on C-4 and C-5. The latter two types of hydrogens are very similar (all are bonded to the aromatic ring) and are expected to have very similar chemical shifts. Although such hydrogens might absorb at the same position in some cases, they *may* have different chemical shifts in other cases because they are not chemically equivalent.

Some cases are a little more subtle. Consider the two hydrogens of the  $\text{CH}_2$  of bromoethane. Are they chemically equivalent? The two imaginary compounds that result from replacing these hydrogens are enantiomers. The hydrogens are termed **enantiotopic** and, like enantiomers, are different only in the presence of something else that is chiral. Thus, they have identical chemical shifts. Two NMR absorptions are expected for this compound: one for the  $\text{CH}_3$  group and one for the  $\text{CH}_2$  group.



How many signals are expected for 2-bromobutane? The methyl groups on each end are obviously different, as is the single H on C-2. At first glance, the two H's on C-3 appear to be identical, but in fact replacement with an imaginary group produces diastereomers. Such hydrogens are termed **diastereotopic** and have different chemical shifts.

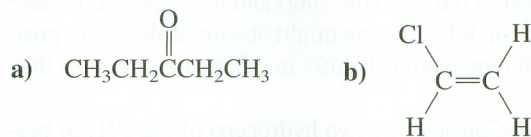


Therefore, there are five different types of hydrogens in 2-bromobutane. However, the chemical shifts of the diastereotopic hydrogens on C-3 will be very similar. In general, the two hydrogens of a  $\text{CH}_2$  group are diastereotopic when a chirality center is present.



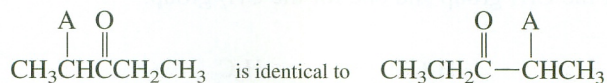
## PRACTICE PROBLEM 14.1

How many absorptions are expected in the  $^1\text{H}$ -NMR spectra of these compounds?



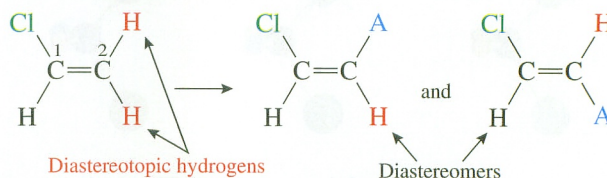
## Solutions

- a) The  $\text{CH}_2$  groups are chemically equivalent because these imaginary compounds are identical.



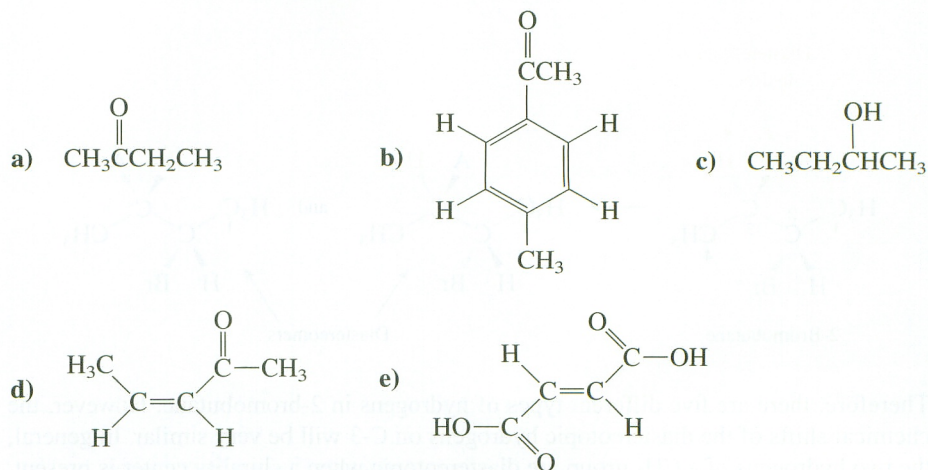
Likewise, the  $\text{CH}_3$  groups are identical. Therefore, there are only two absorptions (ignoring the multiplicities) in the spectrum of 3-pentanone (see Figure 14.1).

- b) The hydrogens on C-2 are diastereotopic because replacing them produces diastereomers. (Remember, *cis*- and *trans*-isomers are one type of diastereomers.) Diastereotopic hydrogens have different chemical shifts, so all three hydrogens of chloroethene are chemically nonequivalent and three signals appear in the spectrum.



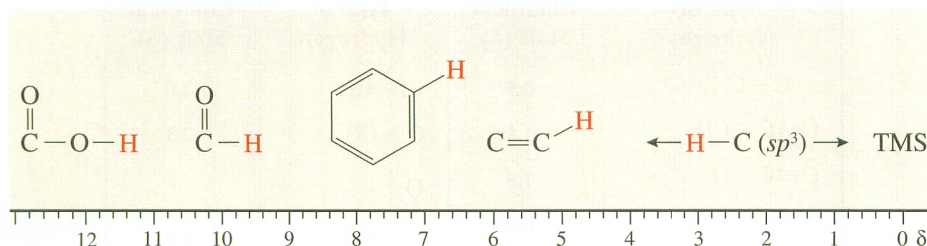
## PROBLEM 14.2

How many absorptions are expected in the  $^1\text{H}$ -NMR spectra of these compounds?





A useful summary of the chemical shift regions where various types of hydrogens appear in NMR spectra is provided by the following diagram:



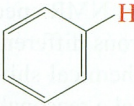
Although the regions overlap somewhat, peak positions often suggest the presence of certain types of hydrogens. For example, a peak in the region of 10 δ is usually due to the hydrogen of an aldehyde, whereas absorptions in the region of 7 to 8 δ suggest the presence of hydrogens on an aromatic ring. These assignments can often be confirmed by examination of the IR spectrum.

More advanced texts on NMR spectroscopy contain detailed tables listing chemical shift values for numerous different kinds of hydrogens. With use of these tables, a good prediction of the chemical shift of almost any proton can be made. Recently, computer programs that make reasonably accurate predictions of chemical shifts have become available. However, we do not need to know chemical shifts that accurately in order to use NMR effectively. Table 14.1 is a much abbreviated version of more complete tables and is sufficient for our needs. It lists the approximate chemical shifts for the most common types of hydrogens. The values in Table 14.1 are for  $\text{CH}_3$  hydrogens (methyl groups);  $\text{CH}_2$  hydrogens (methylene groups) appear about 0.3 δ downfield and  $\text{CH}$  hydrogens (methine groups) appear about 0.7 δ downfield from the  $\text{CH}_3$  values. Also note that the presence of additional functional groups near the hydrogen causes additional downfield shifts. If the additional functional group is attached to the same carbon as the hydrogen under consideration, then the downfield shift is relatively large. The effect decreases rapidly with distance, so if the additional functional group is attached to the carbon adjacent to the carbon to which the hydrogen is attached, the downfield shift is small. If the distance is larger than this, then the shift can be neglected.

Let's see how Table 14.1 can be used to assign chemical shifts in a spectrum to the hydrogens in a compound. Consider 1-propanol. The chemical shift for the hydroxy hydrogen depends on the concentration of the sample and the temperature, so it cannot be predicted exactly, but it is expected to be in the region of 2 to 5 δ. (In this particular sample it actually appeared at 2.3 δ.) The hydrogens on C-1 should appear furthest downfield because they are closest to the electronegative oxygen. From Table 14.1, the predicted position for the hydrogens of  $\text{O}-\text{CH}_3$  is 3.3 δ. The hydrogens on C-1 should appear slightly downfield from this because they are part of a  $\text{CH}_2$  group rather than a  $\text{CH}_3$  group. (Their actual position is 3.5 δ.) The hydrogens on C-2 should appear further upfield because they are not as close to the electronegative oxygen. They are expected to appear somewhat downfield from 0.9 δ, the position for  $\text{C}-\text{CH}_3$  in Table 14.1, because they are part of a  $\text{CH}_2$  group and are also slightly shifted by the oxygen. (Their actual position is 1.5 δ.) The hydrogens on C-3 should appear furthest upfield because they are too far from the hydroxy group to be affected by it. The position predicted from Table 14.1 for  $\text{C}-\text{CH}_3$  is 0.9 δ. (The actual position is 0.9 δ.)

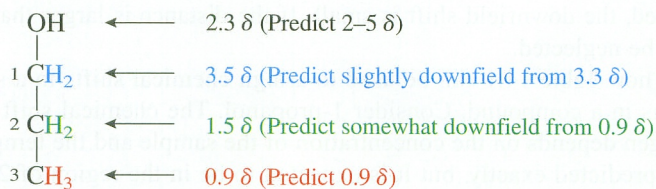


**Table 14.1** Approximate Chemical Shifts of Hydrogens in  $^1\text{H}$ -NMR Spectra

Type of Hydrogen	Chemical Shift ( $\delta$ )	Type of Hydrogen	Chemical Shift ( $\delta$ )
$-\text{C}-\text{CH}_3$	0.9	$\text{Cl}-\text{CH}_3$	3.0
$\text{C}=\text{C}-\text{CH}_3$	1.6	$\text{O}-\text{CH}_3$	3.3
$\text{C}\equiv\text{C}-\text{H}$	1.8	$\text{O}=\text{C}-\text{O}-\text{CH}_3$	3.7
$\text{N}-\text{H}$	1-3	$\text{O}_2\text{N}-\text{CH}_3$	4.1
$\text{O}-\text{H}$	2-5	$\text{F}-\text{CH}_3$	4.2
$\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	2.0	$\text{C}=\text{C}-\text{H}$	5.5-6.5
$\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	2.2		7-8
$\text{N}-\text{CH}_3$	2.2	$\text{O}=\text{C}-\text{H}$	10
$\text{I}-\text{CH}_3$	2.2	$\text{O}=\text{C}-\text{O}-\text{H}$	12
$\text{N}\equiv\text{C}-\text{CH}_3$	2.2		
$\text{Ph}-\text{CH}_3$	2.3		
$\text{Br}-\text{CH}_3$	2.7		

Note that these positions are only approximate. Furthermore, most of these positions are given for  $\text{CH}_3$  groups.

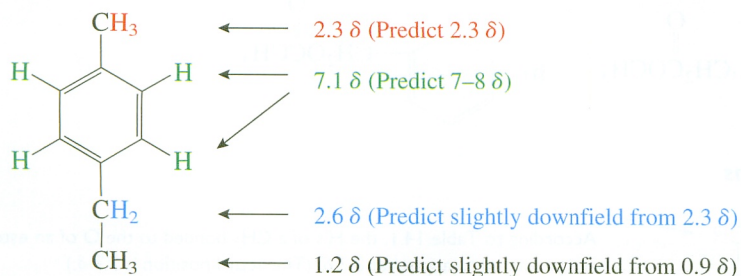
$\text{CH}_2$  groups appear farther downfield by about 0.3 ppm and  $\text{CH}$  groups by about 0.7 ppm.



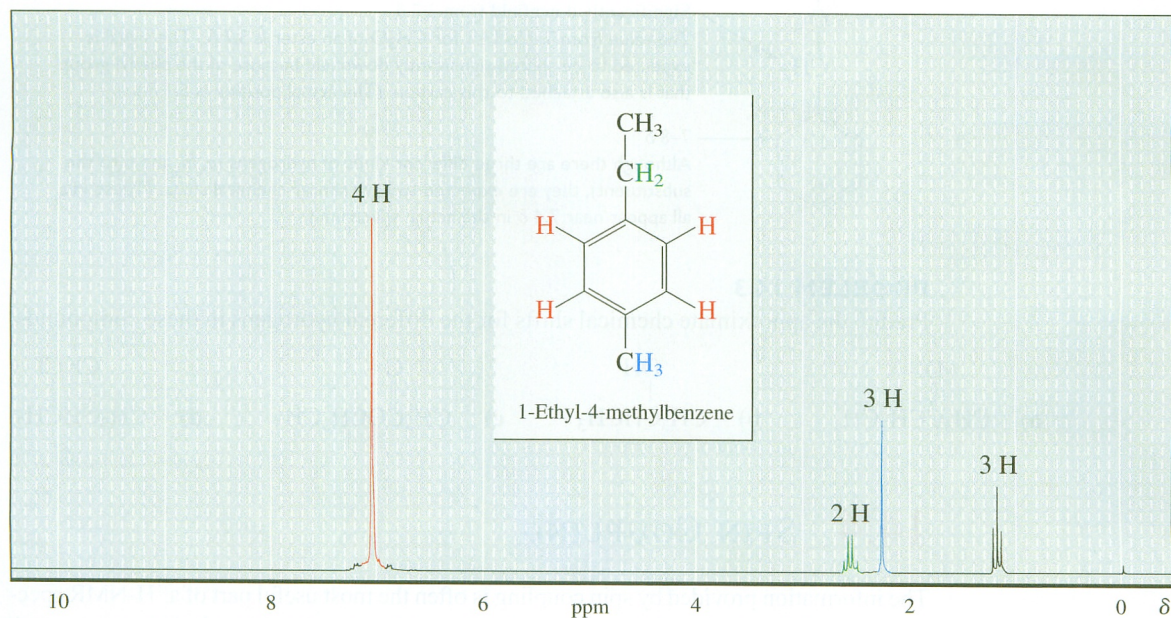
As another example, consider 1-ethyl-4-methylbenzene (*p*-ethyltoluene). This compound has five different types of hydrogens: the  $\text{CH}_3$  attached directly to the ring, the  $\text{CH}_3$  of the ethyl group, the  $\text{CH}_2$  of the ethyl group, the two hydrogens ortho to the methyl group, and the two hydrogens meta to the methyl group. Both types of hydrogens on the benzene ring are predicted to appear in the 7 to 8  $\delta$  region. They should have very similar chemical shifts because the ethyl and methyl groups are both non-polar. (They actually appear at 7.1  $\delta$ .) The methyl group on the aromatic ring is predicted to appear at 2.3  $\delta$ , the value from Table 14.1 for  $\text{Ph}-\text{CH}_3$ . (The actual position is 2.3  $\delta$ .) The  $\text{CH}_2$  of the ethyl group is predicted to appear slightly downfield from



2.3  $\delta$  because it is a  $\text{CH}_2$  group rather than a  $\text{CH}_3$  group. (The actual position is 2.6  $\delta$ .) The  $\text{CH}_3$  of the ethyl group should appear most upfield. It is expected to be shifted slightly downfield from 0.9  $\delta$  ( $\text{C}-\text{CH}_3$ ) due to the nearby aromatic ring. (The actual position is 1.2  $\delta$ .)



The actual NMR spectrum of 1-ethyl-4-methylbenzene is shown in Figure 14.5. Note that the two types of aromatic hydrogens are so similar that they appear as a single peak, at least at the resolution of this spectrometer. Also note that the  $\text{CH}_2$  of the ethyl group appears as a set of four lines, termed a *quartet*, and the  $\text{CH}_3$  of the ethyl group appears as a set of three lines, termed a *triplet*. These multiple peaks result from a process termed *spin coupling*. Analysis of this coupling pattern can be used to tell us that there are three hydrogens near the  $\text{CH}_2$  group and two hydrogens near the  $\text{CH}_3$  group and enables us to determine that the compound contains an ethyl group. Let's see how spin coupling works.



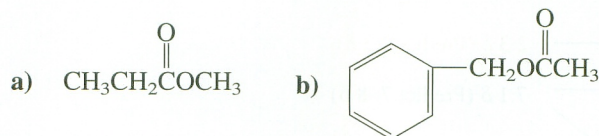
**Figure 14.5**

**THE  $^1\text{H}$ -NMR SPECTRUM OF 1-ETHYL-4-METHYLBENZENE.** The numbers above each group of peaks are the integrals and provide the relative numbers for hydrogens responsible for that group of peaks.

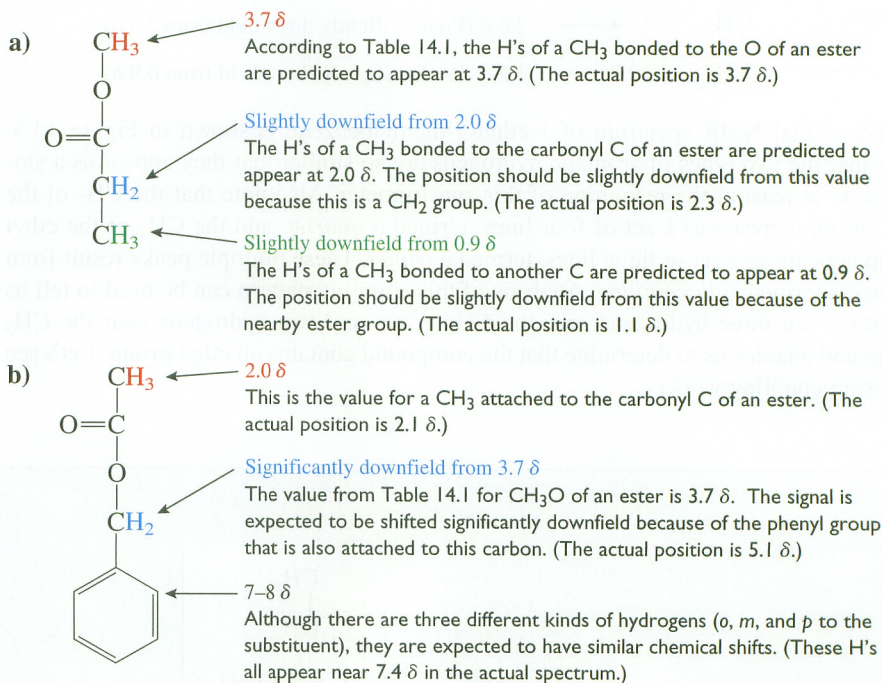


## PRACTICE PROBLEM 14.2

Predict the approximate chemical shifts for the different hydrogens in these compounds.



## Solutions



## PROBLEM 14.3

Predict the approximate chemical shifts for the different hydrogens in these compounds:



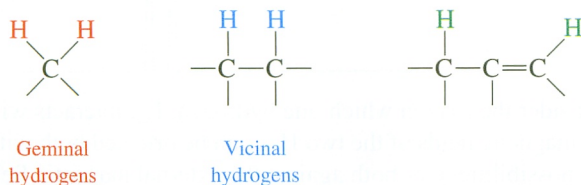
## 14.4 SPIN COUPLING

The information provided by spin coupling is often the most useful part of a  $^1\text{H}$ -NMR spectrum. Recall that each hydrogen in a molecule can be considered as a little bar magnet. A particular hydrogen experiences the small magnetic fields of other nearby hydrogens in addition to the large magnetic field of the external magnet. This results in the splitting of the absorption into multiple peaks. From the multiplicity, or number of peaks, of a signal, it is possible to determine which hydrogens are near the hydrogen responsible for the signal.

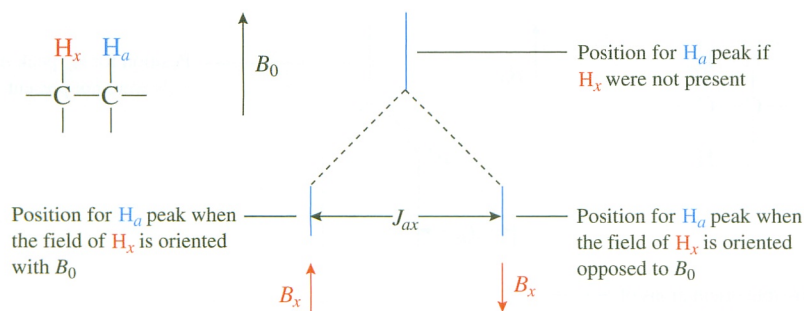
To spin couple, the hydrogens must have different chemical shifts, and they must be relatively close together because the effect of the small magnetic fields of the hydrogens



decreases rapidly with distance. Hydrogens bonded to the same carbon (called **geminal** hydrogens) couple if they are diastereotopic and have different chemical shifts. Hydrogens bonded to adjacent atoms (called **vicinal** hydrogens) also couple. Coupling is not commonly observed between hydrogens that are farther apart than this unless a pi bond is involved, in which case a small coupling between hydrogens separated by three carbons is sometimes observed. Coupling between vicinal hydrogens is by far the most common type.



Let's begin by considering the simplest possible case, in which one hydrogen, call it  $H_a$ , is interacting with one other hydrogen, call it  $H_x$ . In addition to the large external magnetic field,  $H_a$  also experiences the small magnetic field of  $H_x$ . Because the energy difference between the two spin states of a proton is extremely small, the magnetic field of  $H_x$  is oriented in the same direction as the external magnetic field in approximately 50% of the molecules, while the fields are oriented in opposite directions in the other 50% of the molecules. (Basically, the hydrogens in the two spin states are in equilibrium. Because the difference in energy between the two states is so small, the "equilibrium constant" is very close to 1.) The total magnetic field experienced by  $H_a$  is the sum of the field of the external magnet and the field due to the nearby hydrogen,  $H_x$ . In 50% of the molecules the field of  $H_x$  is oriented in the same direction as the external field and increases the field strength at  $H_a$ . In this situation a weaker external magnetic field is needed for the total field strength at  $H_a$  to have the correct value for resonance to occur. This causes the absorption for  $H_a$  to appear at a slightly downfield position. In the other 50% of the molecules the field of  $H_x$  is oriented in opposition to the external magnetic field and subtracts from the field at  $H_a$ . A larger external magnetic field is necessary for resonance and the absorption appears at a slightly upfield position. As a result, the absorption for  $H_a$  appears as two closely spaced peaks, a **doublet**. Both peaks of the doublet have equal areas because the magnetic field orientations that produce them are equally probable. This process is visually represented in the following illustration, called a splitting diagram or a tree diagram:

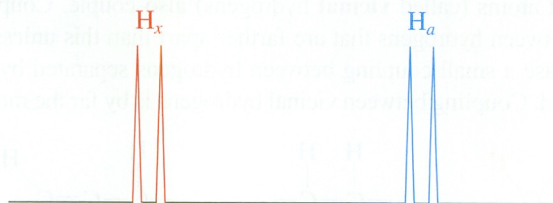


The separation between the two peaks is called the **coupling constant**,  $J_{ax}$ . The coupling constant has units of hertz and does not depend on the operating frequency of the instrument. It ranges from 0 to 20 Hz, with 6 Hz being a typical value for vicinal hydrogens.

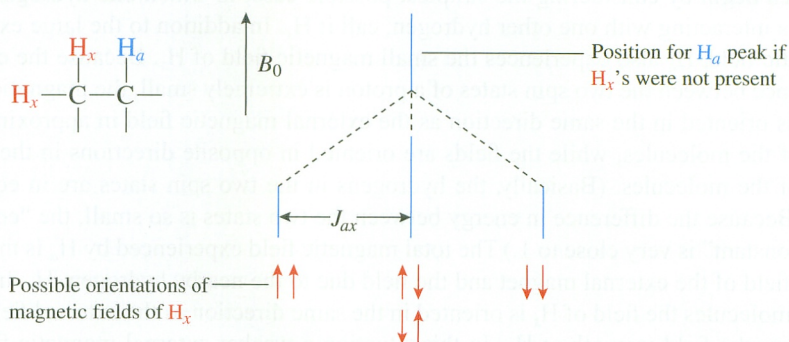
The analysis for  $H_x$  in the preceding example is identical. It is split into a doublet by  $H_a$ , and it is important to note that the coupling constant is exactly the same. The NMR spectrum of this system has two doublets: one for  $H_a$  and one for  $H_x$ . The sepa-



ration between the two peaks of each doublet,  $J_{ax}$ , is identical. The chemical shift of either hydrogen is the center of its doublet.

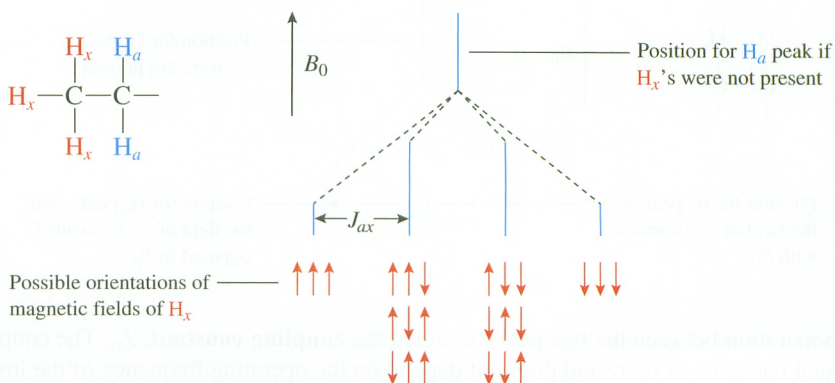


Next let's consider the case in which one hydrogen,  $H_a$ , interacts with two identical protons,  $H_x$ . The magnetic fields of the two  $H_x$ 's can be oriented both with, one with and one against (two possibilities), or both against the external magnetic field. Following is the splitting diagram:



The absorption for  $H_a$  is split into a triplet by the two  $H_x$ 's, with the relative heights of the peaks in a 1:2:1 ratio. The absorption for the  $H_x$ 's is split into a doublet by the single  $H_a$ . The coupling constant,  $J_{ax}$ , is the separation between two adjacent peaks of the triplet or between the peaks of the doublet. An example of such a system is shown in Figure 14.6, the NMR spectrum of 1,1,2-trichloroethane.

As a more complicated example, let's consider the case in which three hydrogens ( $H_x$ ) on one carbon are coupled to two hydrogens ( $H_a$ ) on an adjacent carbon. The following splitting diagram shows that the signal for  $H_a$  is split into four peaks, a quartet, with relative heights of 1:3:3:1:



The signal for  $H_x$  is split into a triplet by the two  $H_a$ 's. The NMR spectrum of bromoethane, shown in Figure 14.7, provides an example of such a system. This pattern of a downfield quartet, due to two hydrogens, and an upfield triplet, due to three hydro-



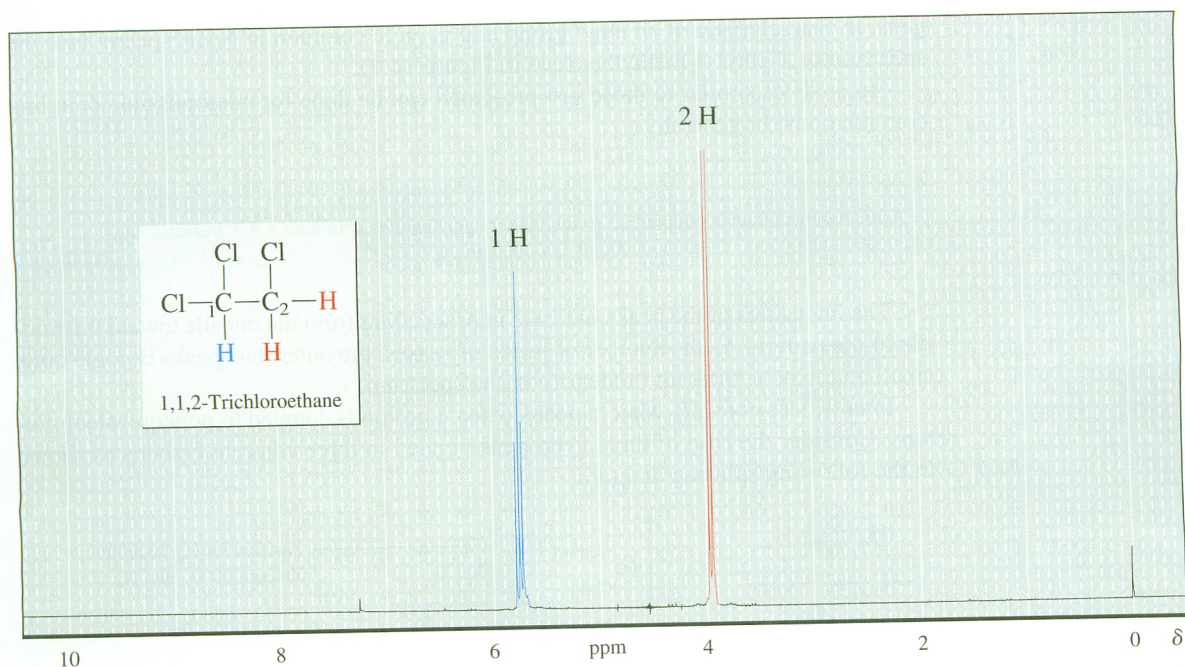


Figure 14.6

**THE  $^1\text{H}$ -NMR SPECTRUM OF 1,1,2-TRICHLOROETHANE.** The hydrogen on C-1 appears farther downfield because there are two electronegative Cl's on this carbon. Its signal is split into a triplet by the two H's on C-2. The signal for the two H's on C-2 is upfield and is split into a doublet by the single H on C-1.

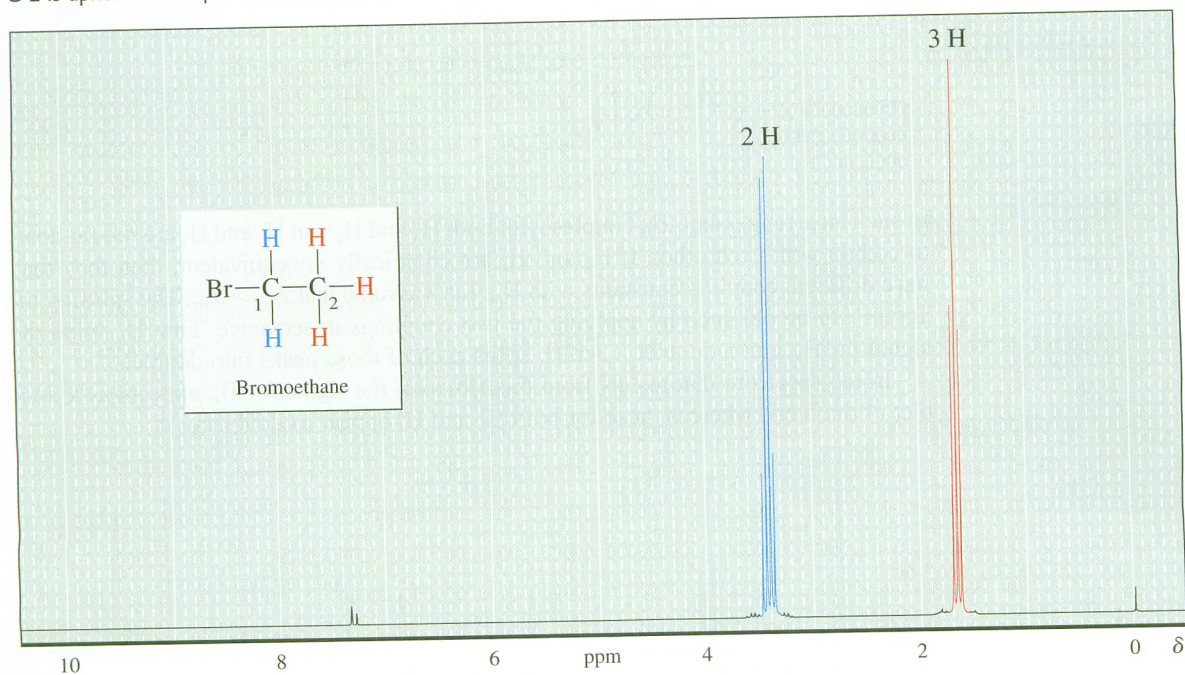


Figure 14.7

**THE  $^1\text{H}$ -NMR SPECTRUM OF BROMOETHANE.** The absorption for the two H's on C-1 is downfield because of the electronegative Br attached to this carbon. The signal is split into a quartet by the three nearby H's on C-2. The signal for the three H's on C-2 is split into a triplet by the two nearby H's on C-1.



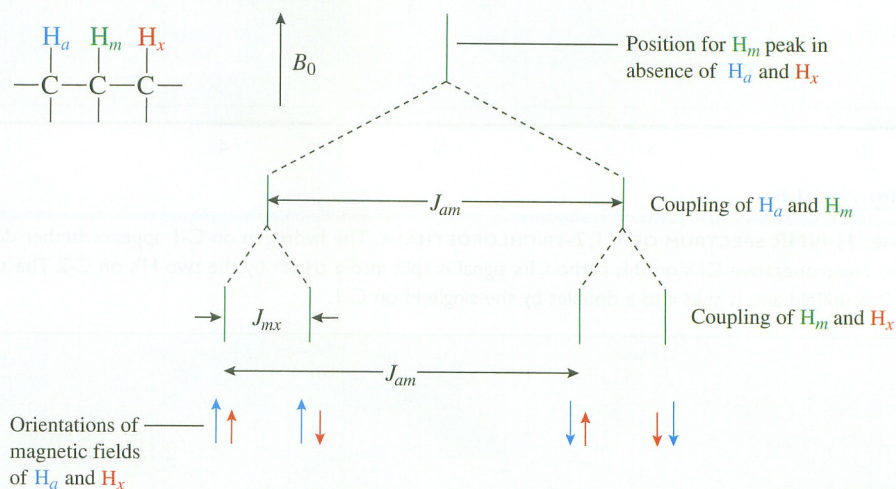
gens, is characteristic of an ethyl group and is quite common in NMR spectra (see the spectrum of 1-ethyl-4-methylbenzene in Figure 14.5).

An analysis similar to those just presented can be done for other possible coupling combinations. In general,

A hydrogen(s) that is coupled to  $n$  equivalent hydrogens is split into  $n + 1$  peaks.

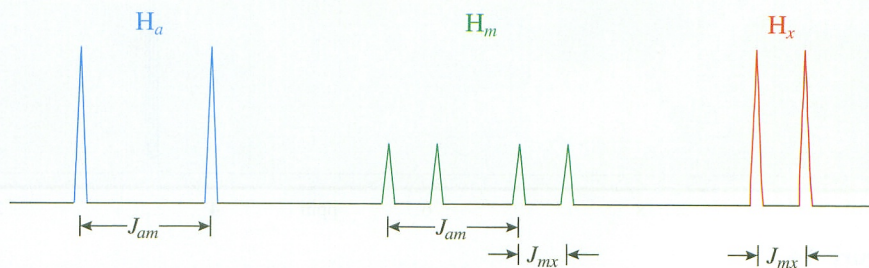
The intensities of the peaks increase in proceeding from the outside toward the middle of the pattern. As the number of peaks increases, the outermost peaks become quite small and may be difficult to identify in the spectrum.

Finally, let's consider what happens when a proton is coupled to nonequivalent protons. Consider the case of three hydrogens bonded to three adjacent carbons as shown in the following splitting diagram:



In such an arrangement,  $H_m$  couples with both  $H_a$  and  $H_x$ , but  $H_a$  and  $H_x$  are too far apart to couple with each other. If  $H_a$  and  $H_x$  are chemically nonequivalent, then they may have different coupling constants with  $H_m$ . Let's assume that  $J_{am} > J_{mx}$ . The splitting diagram can be obtained by applying the two couplings in sequence. First  $H_a$  splits the signal for  $H_m$  into a doublet. Then  $H_x$  splits each of those peaks into doublets.

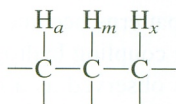
In the spectrum that results from this situation the signal for  $H_m$  appears as a doublet of doublets, whereas those for both  $H_a$  and  $H_x$  appear as doublets.



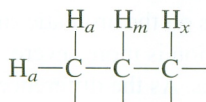


**PROBLEM 14.4**

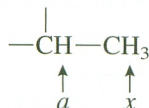
Predict the multiplicity of the absorption for  $H_m$  if  $J_{am} = J_{mx}$ . Explain.

**PROBLEM 14.5**

Construct a tree diagram for the absorption of  $H_m$ . Assume that  $J_{am} < J_{mx}$ .

**PRACTICE PROBLEM 14.3**

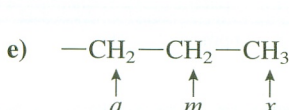
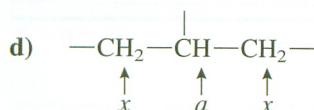
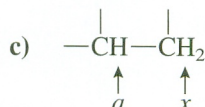
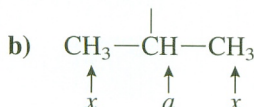
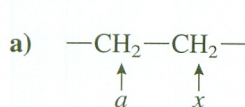
Predict the multiplicities of the absorptions for the hydrogens in this group:

**Solution**

$H_a$  is split by three  $H_x$ 's, so its absorption should appear as a quartet. The  $H_x$ 's are split by one  $H_a$ , so their absorption should appear as a doublet.

**PROBLEM 14.6**

Predict the multiplicities of the absorptions for the hydrogens of these groups. Assume that hydrogens labeled  $a$  are different from those labeled  $x$  but that all of those labeled  $a$  are identical and all of those labeled  $x$  are identical.



Assume  $J_{am} = J_{mx}$

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## 14.5 COMPLEX COUPLING

The splitting patterns that have been discussed so far result from what is called first-order coupling. However, splitting patterns become much more complex as the difference in chemical shifts between the coupling hydrogens becomes smaller. The first indication of this, termed **leaning**, is observed as a distortion of the peak heights of a multiplet. As an example, note how the downfield peak of the triplet in the spectrum of bromoethane (Figure 14.7) is slightly larger than the upfield peak. The triplet “leans” toward the quartet of the other hydrogens. Similarly, the quartet “leans” toward the triplet. However, the deviations from first-order coupling are quite small in this case and the pattern of a triplet and a quartet is easily recognized.

Figure 14.8 shows a spectrum in which the chemical shifts of the coupling hydrogens are closer. The two hydrogens on the aromatic ring spin couple and should appear as doublets. In this case the distortion is more severe, and the outside peaks are considerably smaller than the inside peaks. As the difference in chemical shifts becomes even smaller, the outside peaks become quite small relative to the inside peaks. If more than two hydrogens are involved in such complex coupling, extra peaks appear and the pattern becomes quite complex. Although such patterns, termed **multiplets**, are often encountered, their interpretation is difficult. However, the presence of a multiplet in the spectrum does supply information about the structure in that structural features resulting in complex coupling must be present.

Coupling patterns are more likely to be first order on a NMR instrument with a large magnetic field strength and a high operating frequency because the chemical shift dif-

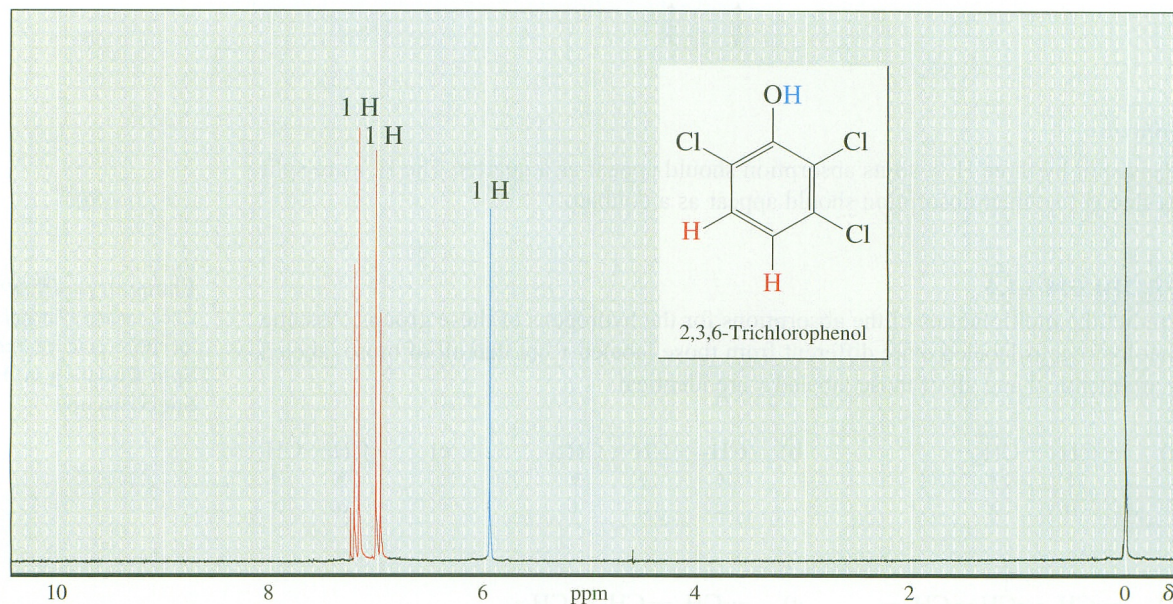


Figure 14.8

**THE  $^1\text{H}$ -NMR SPECTRUM OF 2,3,6-TRICHLOROPHENOL.** The  $\text{H}$  of the hydroxy group appears at  $5.9\ \delta$  and is not split. The two  $\text{H}$ 's on the aromatic ring do couple, and each should appear as a doublet. Because their chemical shifts are similar, the doublets are distorted, the outside peaks being significantly smaller than the inside peaks.

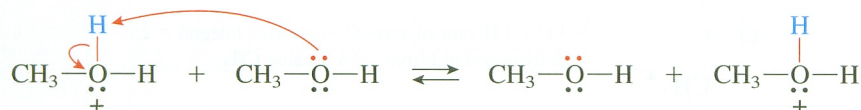


ference, measured in hertz, increases as the magnetic field strength increases. (A chemical shift difference of 0.1  $\delta$  is 20 Hz on an instrument operating at 200 MHz and 40 Hz on an instrument operating at 400 MHz.) As a result, given two different instruments, most spectra will be easier to interpret on the instrument operating at the higher frequency. This is one reason why NMR instruments with larger and larger magnets are constantly being built.

## 14.6 CHEMICAL EXCHANGE

NMR has been compared to a slow camera—that is, one in which the shutter is open for a relatively long period. An object that moves while the camera shutter is open produces a blurred picture. Similarly, a hydrogen that is rapidly switching between two environments appears at a chemical shift that is the average of the chemical shifts of the two environments. For example, the axial and equatorial hydrogens of cyclohexane have different chemical shifts. However, at room temperature they are interchanging so rapidly by the ring-flipping process that the NMR spectrum of cyclohexane shows only one peak at the average of the two positions. If the spectrum is run at very low temperature, the ring-flips can be slowed enough that separate peaks appear for the two types of hydrogens.

The spectrum of methanol,  $\text{CH}_3\text{OH}$ , provides another example of this effect. The hydroxy hydrogen is expected to appear as a quartet and the methyl hydrogens as a doublet if coupling occurs. However, this coupling is not observed unless the methanol is extremely pure. A trace of acid (or base) that is present in normal samples of this alcohol causes a rapid exchange of the hydroxy hydrogens by the following acid–base reaction:



This reaction is so rapid that during the time that the NMR is examining the hydrogens of the methyl group, a large number of different hydrogens have been bonded to the oxygen. Because 50% of these hydrogens have their magnetic fields oriented in one direction and 50% have them oriented in the opposite direction, the average field is zero. Therefore, the peak due to the methyl group is not split, nor is the peak due to the hydroxy hydrogen. The spectrum shows two singlets.

In general, hydrogens on oxygen or nitrogen are subject to this rapid exchange process and do not couple to nearby hydrogens. However, caution must be exercised because coupling does occur in some samples.

## 14.7 DEUTERIUM

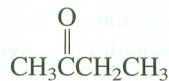
Although the nucleus of deuterium (the isotope of hydrogen with an atomic mass of 2) has spin quantum states, its magnetogyric ratio is different from that of hydrogen, so it does not appear in a  $^1\text{H}$ -NMR spectrum. In addition, spin coupling between deu-



terium and hydrogen is very small, so splitting is usually negligible. Therefore, deuterium is essentially invisible in  $^1\text{H}$ -NMR spectra, a useful feature. For example, the solvents used to dissolve samples for NMR spectra should not have any signals. Carbon tetrachloride can be used, but it is not very polar and many organic compounds are not very soluble in it. The deuterium analog of chloroform,  $\text{CDCl}_3$ , is a more versatile solvent and is commonly used to obtain NMR spectra. More expensive solvents, such as the deuterated analogs of acetone, benzene, or DMSO, are available for special applications. Deuterium is also useful as a label in the study of organic reaction mechanisms. A particular hydrogen in the reactant is replaced with deuterium. Then NMR spectroscopy is used to determine the position of this deuterium in the product by noting which signal is missing.

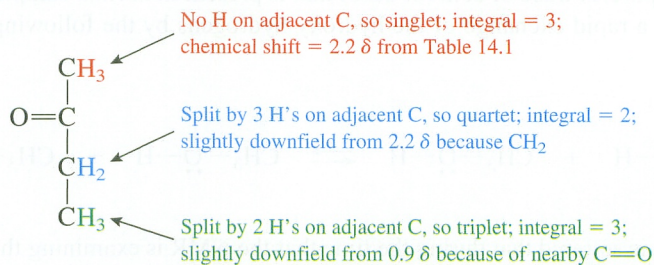
### PRACTICE PROBLEM 14.4

Predict the  $^1\text{H}$ -NMR spectrum of 2-butanone. Include the approximate chemical shift, multiplicity, and integral for each type of hydrogen.



2-Butanone

#### Solution



### PROBLEM 14.7

Predict the  $^1\text{H}$ -NMR spectra of these compounds. Include the approximate chemical shift, multiplicity, and integral for each type of hydrogen.

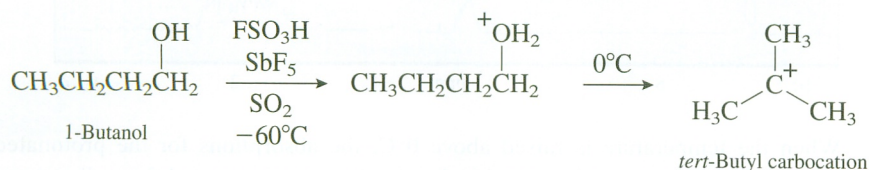
- a)  $\text{CH}_3\text{CH}_2\text{OH}$       b)  $\text{CH}_3\overset{\text{Cl}}{\underset{|}{\text{CH}}}\text{CH}_3$       c)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
- d)  $\text{CH}_2\text{CH}_2\text{NO}_2$       e)  $\text{CH}_3\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_3$       f)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- g)  $\text{CH}_3\text{CHCl}_2$



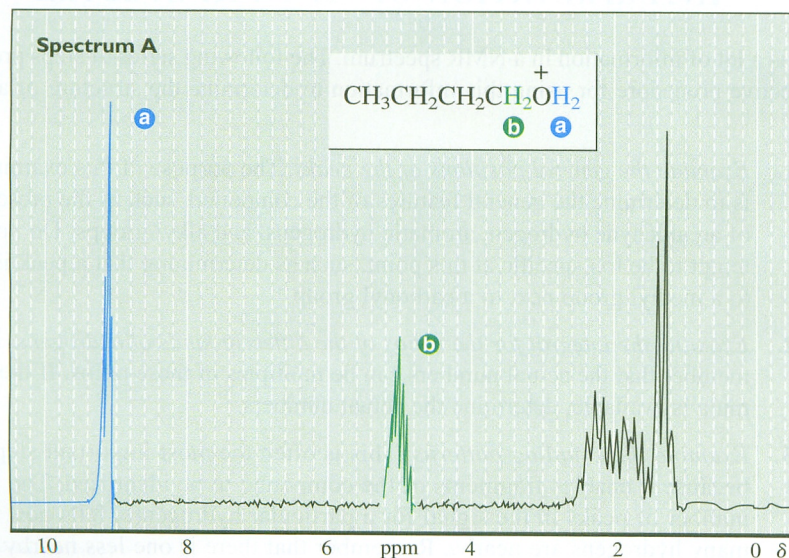
## Focus On

### NMR Spectroscopy of Carbocations in Superacid

The Focus On box in Chapter 8 on page 298 showed that when carbocations are generated in superacid solution, they undergo extensive rearrangements, usually forming a relatively stable tertiary carbocation. As an example, when 1-butanol is dissolved in superacid at  $-60^{\circ}\text{C}$ , the protonated alcohol is formed. Water does not leave at this temperature because the carbocation that would be formed is primary. When the temperature is raised to  $0^{\circ}\text{C}$ , water leaves but the carbocation rearranges rapidly to the more stable *tert*-butyl carbocation:

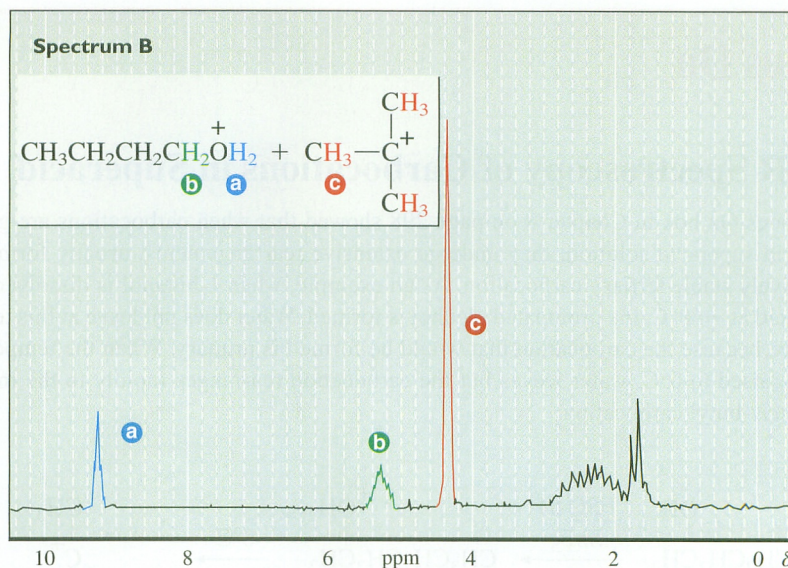


$^1\text{H}$ -NMR spectroscopy was used to conduct this investigation. Spectrum A shows the spectrum of 1-butanol dissolved in superacid at  $-60^{\circ}\text{C}$ . **a** The two hydrogens on the oxygen of the protonated alcohol appear as a triplet near  $9.5\ \delta$ . **b** The two hydrogens on C-1 are shifted downfield by the electron-withdrawing positive oxygen and appear near  $5\ \delta$ . They are split by the two hydrogens on the oxygen and the two hydrogens on C-2 and so should appear as a triplet of triplets. These overlap so that only seven lines are observed.



Continued





When the temperature is raised above  $0^\circ\text{C}$ , the absorptions for the protonated alcohol begin to decrease and a new signal **c** begins to appear near  $4\delta$  (see Spectrum B). This is the absorption due to the *tert*-butyl carbocation, in which all of the hydrogens are identical. No absorptions that could be attributed to other carbocations are observed, indicating that the rearrangement to the *tert*-butyl carbocation is very fast.

## 14.8 INTERPRETATION OF $^1\text{H}$ -NMR SPECTRA

There is a lot of information in a NMR spectrum. The following series of steps provides an effective procedure for using this information to determine the structure of a compound:

- Step 1.** *Examine the general positions of the peaks.* The purpose of this examination is to determine the general features of the compound, such as the presence of an aldehyde hydrogen, aromatic hydrogens, and alkyl groups. Do not attempt to be too specific at this point, such as determining that a peak is due to a methyl group next to a carbonyl group.
- Step 2.** *Examine the integral for the ratios of the different kinds of hydrogens.* Remember that the actual numbers can be multiples of these ratios. If the formula is available, determine the actual numbers.
- Step 3.** *Examine the coupling patterns.* This is often the most important step because it enables fragments of the compound to be identified. The number of peaks in the signal for a particular hydrogen(s) tells how many hydrogens are nearby. Remember that there is one less nearby hydrogen than the number of peaks; that is, if a signal is split into four



lines (a quartet), then there are three nearby hydrogens. Keep in mind that coupling is reciprocal; that is, if there is a signal for two hydrogens split into a doublet because of coupling to one hydrogen, then somewhere else in the spectrum there must appear a signal for this one hydrogen that is split into a triplet by the two hydrogens. (Actually, this signal could contain more than three lines if the one hydrogen is also coupled to other hydrogens.)

**Step 4.** *Construct a tentative structure.* At this point, various fragments have been identified from the coupling patterns, the chemical shifts, the IR spectrum (if available), the formula, and so on. Assemble these fragments into a tentative structure.

**Step 5.** *Determine whether all of the information is consistent with this structure.* See whether the chemical shifts are consistent for each type of hydrogen. Check the multiplicity and integral of each type. Look for any different way to assemble the fragments that would be consistent with all of the data.

Let's try an example. Figure 14.9 shows the NMR spectrum of an unknown compound with the formula  $\text{C}_9\text{H}_{12}$ . When the formula is known, it is useful to first calculate the degree of unsaturation. In this case the DU is 4, so the compound contains a total of four rings and pi bonds. Examination of the general positions shows a multiplet in the aromatic region (7.2  $\delta$ ) and two multiplets upfield in the alkyl region. The integral indicates that these hydrogens are in a 5:1:6 ratio. Because there are 12 hydrogens, the

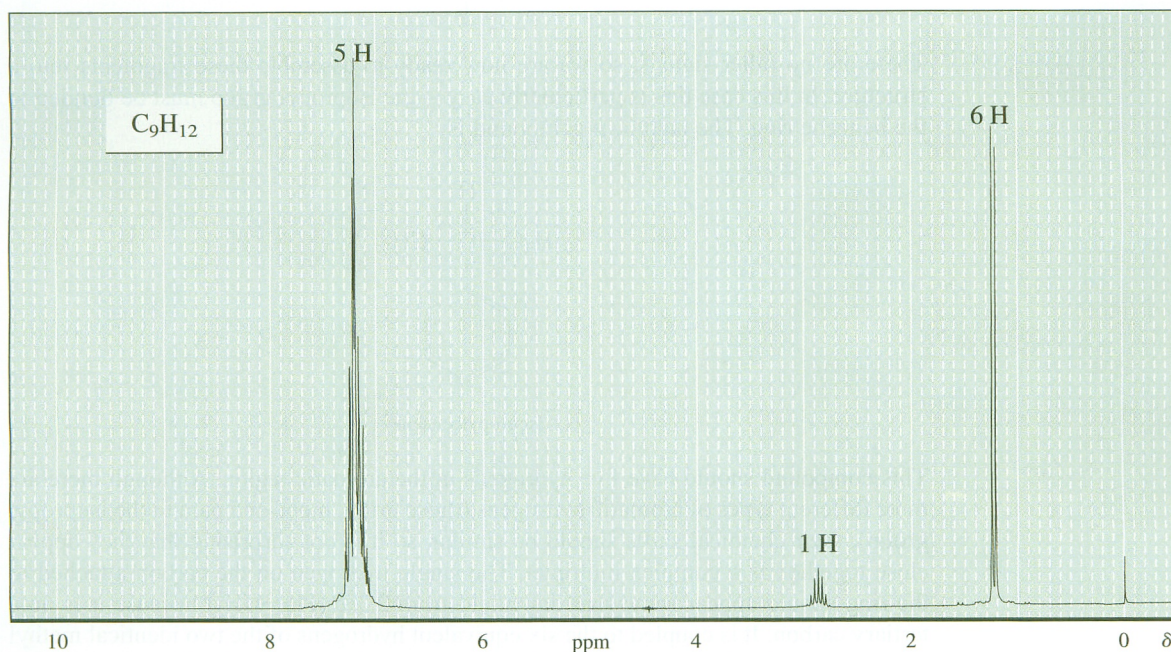
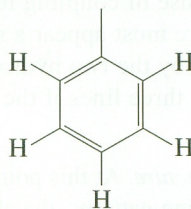


Figure 14.9

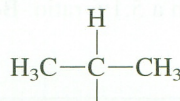
THE  $^1\text{H}$ -NMR SPECTRUM OF AN UNKNOWN COMPOUND WITH THE FORMULA  $\text{C}_9\text{H}_{12}$ .



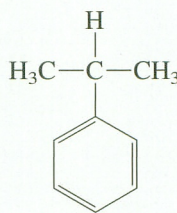
actual numbers must be 5, 1, and 6. The five hydrogens in the aromatic region suggest the presence of a monosubstituted benzene ring:



(Note that a benzene ring has three pi bonds and one ring, accounting for the DU of 4.) The substituent on the ring must be nonpolar so that all five of the hydrogens have similar chemical shifts. The signal at 2.9  $\delta$ , resulting from a single hydrogen, contains seven lines (a septet). It must be coupled to six nearby hydrogens. (When a signal has a large number of lines, it is often difficult to count the exact number because the outside lines are so small. It is difficult to be sure that the small outermost lines are real and not part of the noise in the baseline. However, internal consistency requires the presence of seven lines here, as will become apparent shortly.) The signal at 1.2  $\delta$ , due to six identical hydrogens, is a doublet, so these hydrogens must be coupled to a single hydrogen. Note the internal consistency: one hydrogen at 2.9  $\delta$  coupled to six and six hydrogens at 1.2  $\delta$  coupled to one. From this information an isopropyl fragment must be present:



There are no other signals, so we are now ready to assemble these fragments into a structure. In this case this is particularly easy—the isopropyl group must be bonded to the benzene ring. The unknown compound is



Isopropylbenzene

This compound should have five hydrogens in the aromatic region. Although there are three different types of aromatic hydrogens (those ortho, meta, and para to the isopropyl group), their chemical shifts should be similar, so it is not surprising that they appear close together as a complex multiplet. The single hydrogen on the carbon attached to the ring should appear somewhat downfield from 2.3  $\delta$  ( $\text{Ph}-\text{CH}_3$ ) because it is on a tertiary carbon. It is coupled to the six equivalent hydrogens of the two identical methyl groups, so it should appear as a septet. The methyl hydrogens should appear slightly downfield from 0.9  $\delta$  ( $\text{C}-\text{CH}_3$ ), due to the effect of the nearby phenyl group. They are coupled to a single proton, so they should appear as a doublet. All of the features of the spectrum are consistent with this structure.



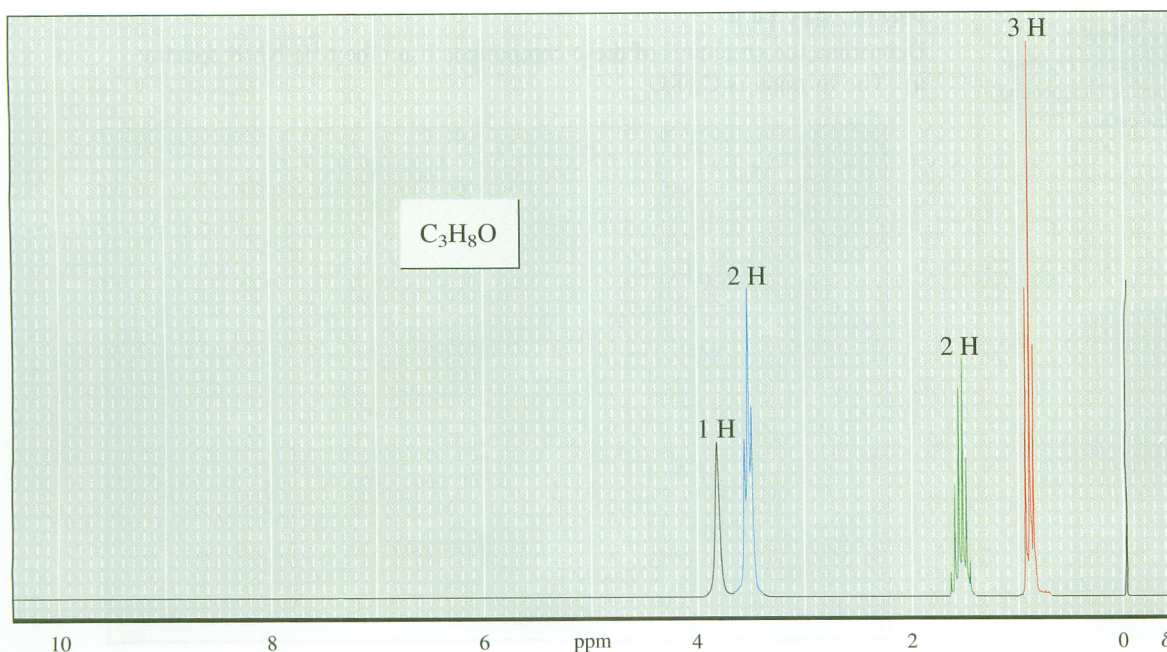


Figure 14.10

**THE  $^1\text{H}$ -NMR SPECTRUM OF AN UNKNOWN COMPOUND,  $\text{C}_3\text{H}_8\text{O}$ .** This compound shows an OH in its IR spectrum. Its DU equals 0. Examination of its NMR spectrum indicates only alkyl-type H's. The integral provides the actual number of H's in this case, since they total eight. The broad singlet due to one H at  $3.8\ \delta$  is probably due to the hydroxy H, which is not coupled due to rapid chemical exchange. The two H's at  $3.5\ \delta$  appear as a triplet and must be coupled to two H's—the two H's at  $1.5\ \delta$ . The three H's at  $0.9\ \delta$  appear as triplet and must be coupled to the two H's at  $1.5\ \delta$  also. If this is the case, then the two H's at  $1.5\ \delta$  are coupled to  $3 + 2 = 5$  H's and should appear as six lines, a sextet. This information allows the fragment  $\text{CH}_2\text{CH}_2\text{CH}_3$  to be written. Combining this with the HO indicates that the unknown is 1-propanol. The predicted chemical shifts (see page 554) agree well with those in the spectrum.

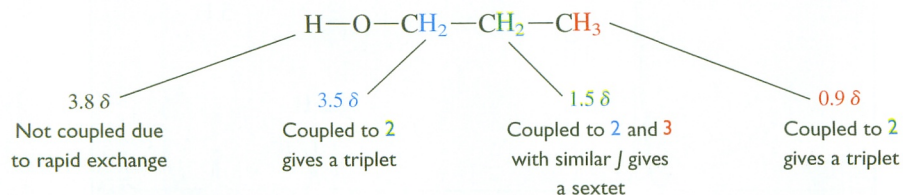


Figure 14.10 provides another example. An interesting feature of this case is the multiplicity of the signal for the center  $\text{CH}_2$  group. These hydrogens are coupled to two hydrogens on one side and three different hydrogens on the other side and could appear as  $3 \times 4 = 12$  lines. However, because the coupling constants are very similar, the signal behaves as though there were five identical hydrogens doing the splitting, and it appears as six lines. This is typical for coupling involving hydrogens on alkyl chains with minimum conformational restrictions.

Problems that use both IR and NMR spectra to determine the identity of unknowns are provided in Section 14.10.

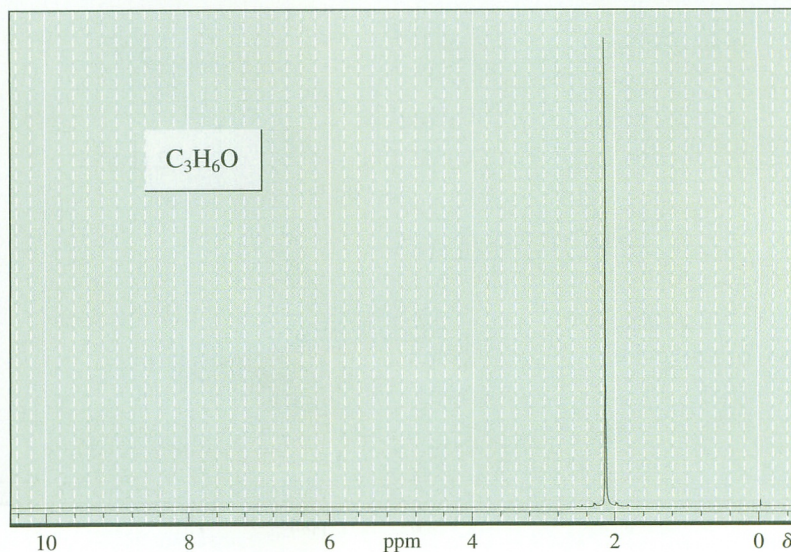


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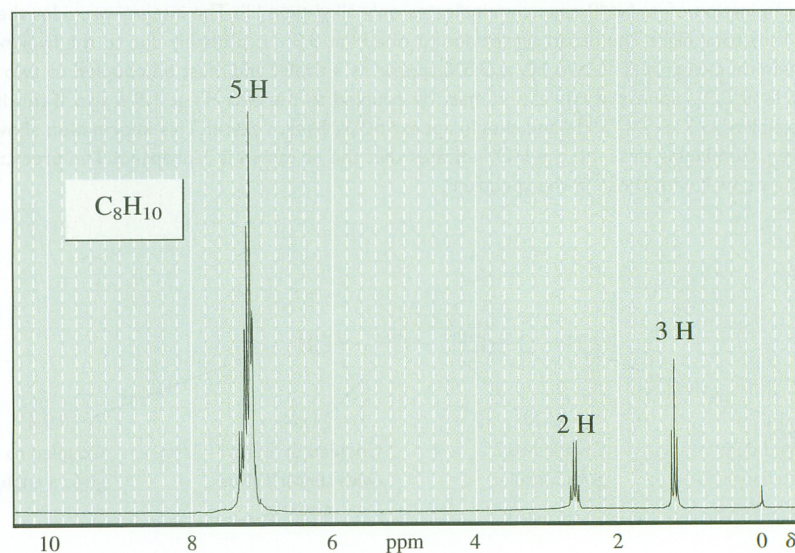
**PROBLEM 14.8**

Determine the structures of these compounds from their <sup>1</sup>H-NMR spectra:

- a) The formula is C<sub>3</sub>H<sub>6</sub>O.

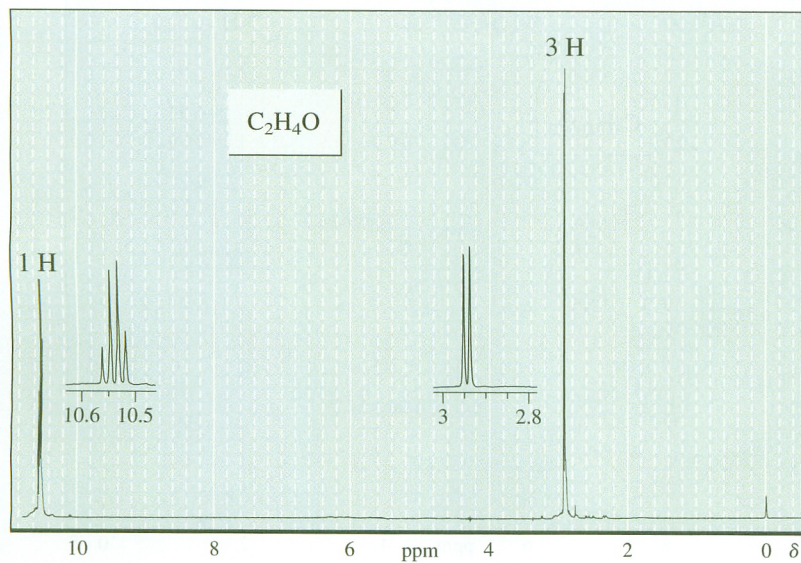


- b) The formula is C<sub>8</sub>H<sub>10</sub>.

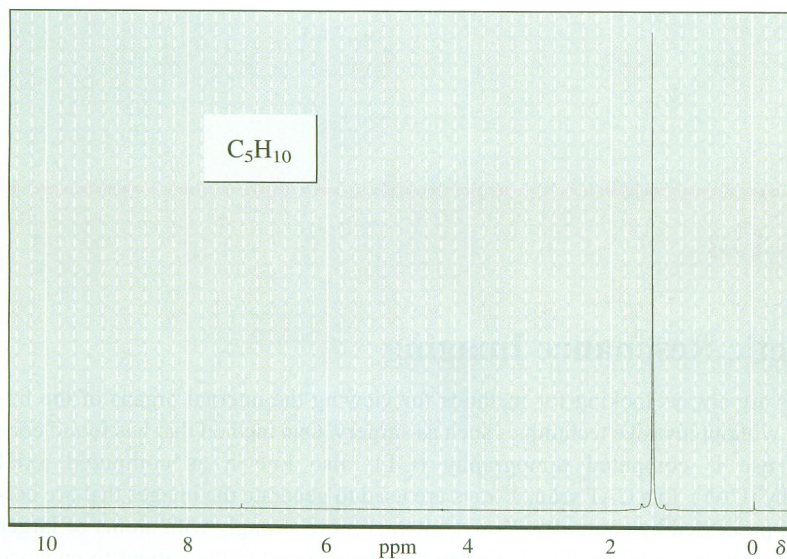




c) The formula is  $\text{C}_2\text{H}_4\text{O}$ .

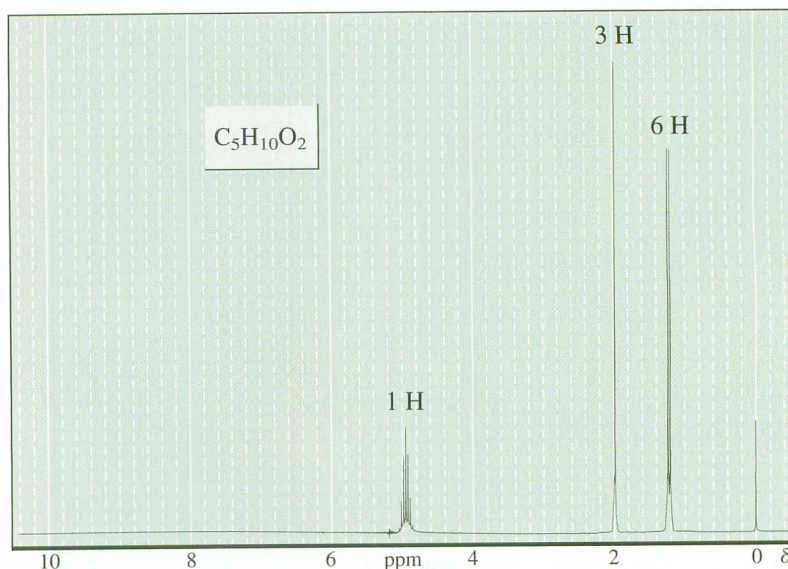


d) The formula is  $\text{C}_5\text{H}_{10}$ .





e) The formula is  $C_5H_{10}O_2$ .



## Focus On

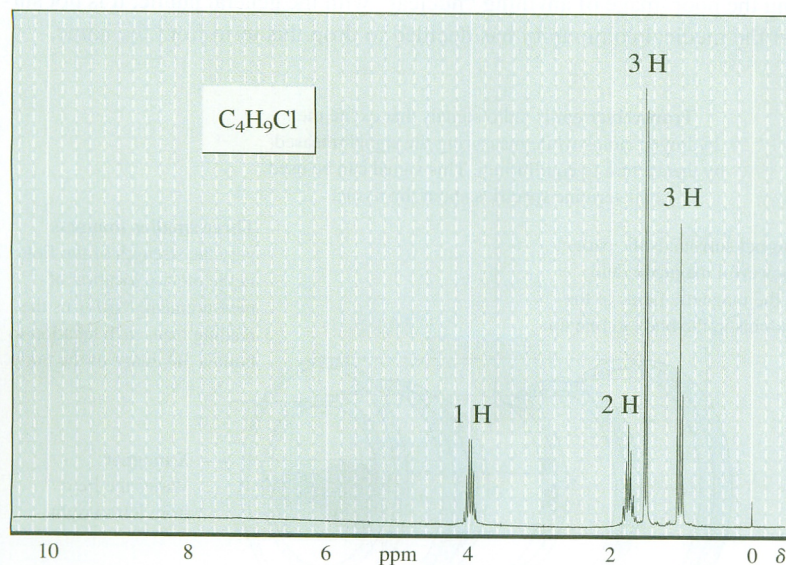
### Magnetic Resonance Imaging

Physicians are always looking for methods for viewing the internal organs of the human body without invasive techniques such as surgery. One method that has found considerable use is computed tomography (CT), also known as computed axial tomography (CAT). In a CAT scan, X-rays are used to generate the images that are collected and processed by computer. X-rays interact more strongly with atoms of larger atomic mass, so imaging agents must often be administered to the patient to enhance the pictures of soft tissues, which are composed primarily of C, H, N, and O. Another potential disadvantage of the CAT technique is the high energy of the radiation that is used. X-rays are called ionizing radiation because they have enough energy to eject electrons from the orbitals of atoms. Chemical reactions caused by the resulting ions can cause damage to living tissue. Although ionizing radiation techniques pose little hazard if done properly, techniques using less energetic radiation are desirable.

Magnetic resonance imaging (MRI) is a newer technique based on the same principles as  $^1H$ -NMR. The 2003 Nobel Prize in physiology or medicine was awarded to Paul C.



f) The formula is  $\text{C}_4\text{H}_9\text{Cl}$ .

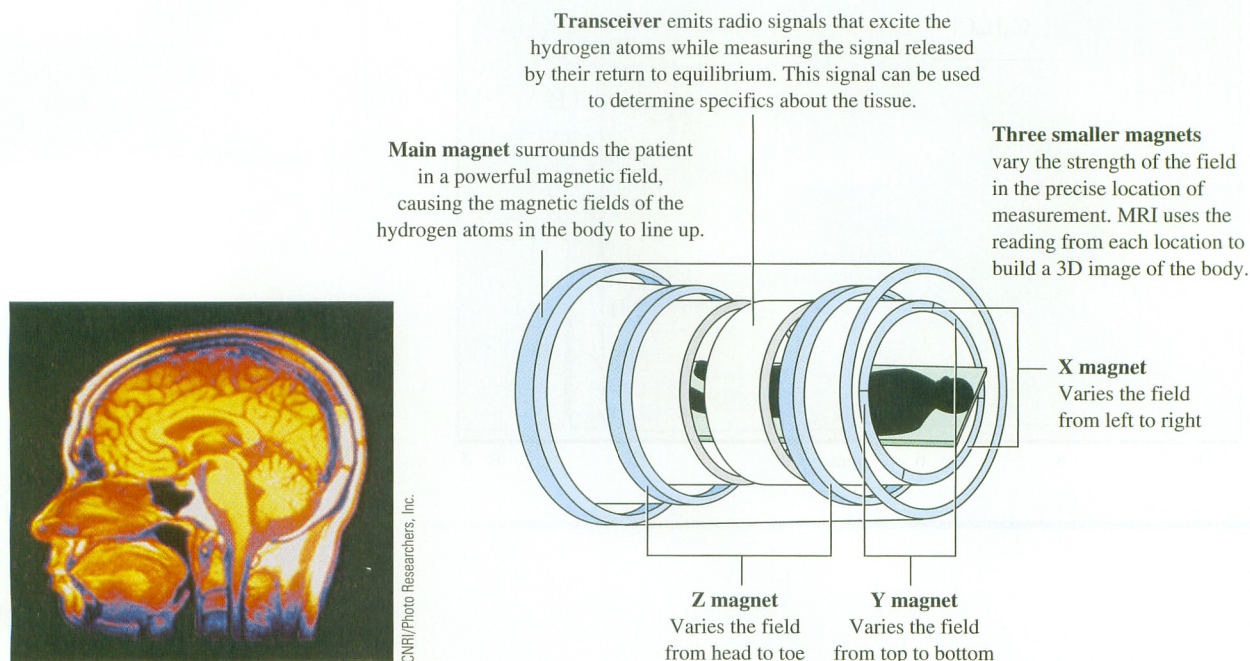


Lauterbur and Sir Peter Mansfield for their discoveries concerning this technique. The patient is placed within the field of a huge magnet and radio-frequency radiation is used to excite hydrogen nuclei to their higher-energy spin state. (The low energy of this radiation poses no danger to the patient.) The magnetic field of an MRI instrument is not nearly as uniform as that of a NMR spectrometer, so the signal for the protons is a very broad peak rather than the individual multiplets that we have seen in a NMR spectrum. The instrument detects differences in the intensity of the proton signal. The intensity depends on the concentration of hydrogens in the small area being sampled and on the “relaxation times,” that is, the time that it takes a hydrogen in the higher-energy spin state to return to the ground state. Both of these factors cause different environments, such as fluids, tissues, and even diseased tissues, to produce signals of different intensities. The data are gathered by a computer, which produces a map or picture of the intensities. Because MRI is looking at hydrogens, it gives a particularly good image of soft tissue and therefore complements CAT. The accompanying figure shows a MRI image of a human skull.

*Continued*



Actually, this technique should be called nuclear magnetic resonance imaging. Considering the poor image of anything “nuclear” with the general public, it is not surprising that the medical community has decided to drop this term from the name.



## 14.9 CARBON-13 MAGNETIC RESONANCE SPECTROSCOPY

The isotope of carbon with seven neutrons,  $^{13}\text{C}$ , composes about 1.1% of carbon atoms. It is similar to hydrogen in that it has two nuclear spin states of different energy when it is in an external magnetic field. The spectroscopy that is done using this nucleus,  $^{13}\text{C}$ -NMR, provides direct information about the carbon chains in the compound, information that is often complementary to that obtained from  $^1\text{H}$ -NMR spectroscopy.

Figure 14.11 shows the  $^{13}\text{C}$ -NMR spectrum of 3-buten-2-one. In contrast to  $^1\text{H}$ -NMR, the peak for each carbon appears as a sharp singlet. Chemical shifts are measured by using the carbons of TMS as a standard. The chemical shift range is much larger in  $^{13}\text{C}$ -NMR than in  $^1\text{H}$ -NMR—peaks appear as far as 240 ppm downfield from TMS. Therefore, overlap of peaks resulting from different carbons occurs much less often than overlap of hydrogen peaks. It is usually possible to count all of the different types of carbons in a compound by examination of its  $^{13}\text{C}$ -NMR spectrum.



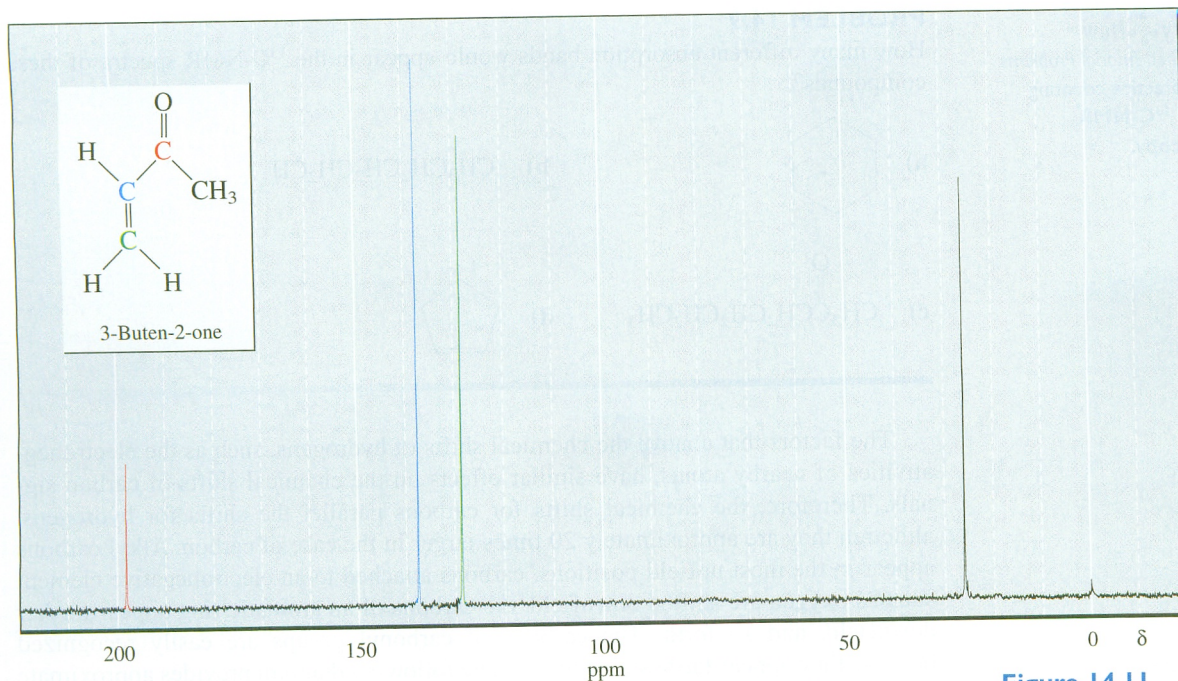
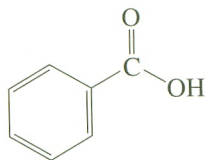


Figure 14.11

THE  $^{13}\text{C}$ -NMR SPECTRUM  
OF 3-BUTEN-2-ONE.

### PRACTICE PROBLEM 14.5

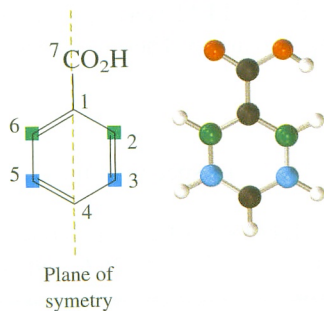
How many different absorption bands would appear in the  $^{13}\text{C}$ -NMR spectrum of benzoic acid?



Benzoic acid

### Solution

The compound has a plane of symmetry, so some carbons are chemically equivalent to others. There are five different types of carbons, C-7, C-1, C-2 = C-6, C-3 = C-5, and C-4, so there are five absorptions in the  $^{13}\text{C}$ -NMR spectrum.

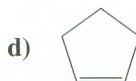
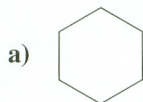




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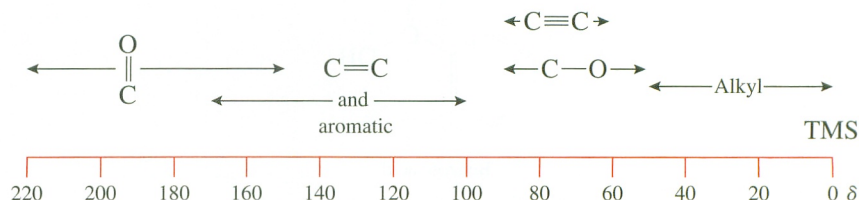
**PROBLEM 14.9**

How many different absorption bands would appear in the  $^{13}\text{C}$ -NMR spectra of these compounds?



The factors that control the chemical shifts of hydrogens, such as the electronegativities of nearby atoms, have similar effects on the chemical shifts of carbon signals. Therefore, the chemical shifts for carbons parallel the shifts for hydrogens, although they are approximately 20 times larger in the case of carbon. Alkyl carbons appear in the most upfield positions, carbons attached to an electronegative element such as oxygen are shifted downfield, the carbons of an aromatic ring appear farther downfield, and so forth. The carbons of carbonyl groups are easily recognized because they appear farthest downfield. The following diagram provides approximate chemical shifts for the various types of carbons that are encountered in organic compounds.

Note the similarity of this diagram to that for proton chemical shifts on page 553, with the difference that the carbon chemical shifts are about 20 times larger than the hydrogen chemical shifts. Table 14.2 provides a somewhat more detailed summary of carbon chemical shifts.



Numerous tables, empirical equations, and even computer programs are available that enable the chemical shifts of the carbons of most compounds to be predicted rather accurately. However, it is possible to assign the carbons responsible for the peaks in many spectra based only on the limited information presented here. For example, the peak at 198.0  $\delta$  in Figure 14.11 is assigned to the carbonyl carbon, and the peak at 26.1  $\delta$  is due to the methyl carbon. The two alkene carbons appear at 137.5 and 128.5  $\delta$ .

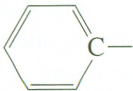
**PROBLEM 14.10**

Assign the absorptions in the  $^{13}\text{C}$ -NMR spectra of these compounds to the appropriate carbons:

- a) 1-Butanol; absorptions at 61.4, 35.0, 19.1, and 13.6  $\delta$   
 b) Cyclohexanone; absorptions at 209.7, 41.9, 26.6, and 24.6  $\delta$



**Table 14.2** Approximate Chemical Shifts of Carbons in  $^{13}\text{C}$ -NMR Spectra

Type of Carbon	Chemical Shift ( $\delta$ )
1° Alkyl, $\text{RCH}_3$	0–40
2° Alkyl, $\text{RCH}_2\text{R}$	10–50
3° Alkyl, $\text{RCHR}_2$	15–50
Alkyl halide or amine, $\begin{array}{c}   \\ -\text{C}-\text{X} \\   \end{array}$ ( $\text{X} = \text{Cl}, \text{Br}, \text{or } \text{N}-$ )	10–65
Alcohol or ether, $\begin{array}{c}   \\ -\text{C}-\text{O} \\   \end{array}$	50–90
Alkyne, $-\text{C}\equiv$	60–90
Alkene, $\begin{array}{c} \diagup \\ \text{C}=\diagdown \end{array}$	100–170
Aryl, 	100–170
Nitriles, $-\text{C}\equiv\text{N}$	120–130
Amides, $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{N}- \\   \end{array}$	150–180
Carboxylic acids, esters, $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{O} \end{array}$	160–185
Aldehydes, ketones, $\begin{array}{c} \text{O} \\    \\ -\text{C}- \end{array}$	180–215

Let's now deal with the issue of spin coupling in  $^{13}\text{C}$ -NMR spectra. No  $^{13}\text{C}-^{13}\text{C}$  coupling is observed because of the low natural abundance of this isotope. A particular  $^{13}\text{C}$  has another  $^{13}\text{C}$  adjacent to it in only 1% of the situations, so the split peaks are very small in comparison to the unsplit peaks. However, coupling between carbon and hydrogen is strong and occurs even when they are separated by several intervening bonds. Because the resulting spectra are usually complex and difficult to interpret, C—H coupling is removed by a technique called **broadband decoupling**. In this technique, as the carbon spectrum is being obtained, the sample is simultaneously irradiated with a band of radio-frequency radiation that excites all of the hydrogens. This causes each of the hydrogens to flip rapidly between its two spin states, so its two magnetic field orientations average to zero. No coupling occurs with the carbon and each peak appears as a singlet.

Several techniques have been developed that enable the number of hydrogens attached to the carbon to be determined. An older technique, called **off-resonance decoupling**, allows hydrogens and carbons that are directly bonded to couple but removes any longer-range coupling. In an off-resonance decoupled spectrum, a  $\text{CH}_3$  appears as



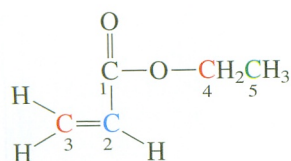
a quartet, a  $\text{CH}_2$  appears as a triplet, a  $\text{CH}$  appears as a doublet, and a  $\text{C}$  that has no hydrogens bonded to it appears as a singlet. A newer and more convenient technique, called **DEPT-NMR** (distortionless enhancement by polarization transfer), also allows the determination of the number of hydrogens attached to each carbon. In a DEPT experiment, three spectra are obtained. One is a normal broadband decoupled spectrum. Another spectrum (DEPT  $90^\circ$  spectrum) is obtained under special conditions in which only carbons bonded to a single hydrogen ( $\text{CH}$ 's) appear. A third spectrum (DEPT  $135^\circ$  spectrum) is obtained under conditions in which  $\text{CH}$ 's and  $\text{CH}_3$ 's appear as positive absorptions and  $\text{CH}_2$ 's appear as negative absorptions. By combining the information in these spectra, each peak can be assigned as resulting from a  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$ , or  $\text{C}$  group. Thus, signals that appear only in the broadband decoupled spectrum are due to  $\text{C}$ 's with no attached  $\text{H}$ 's. Signals that appear in the DEPT  $90^\circ$  spectrum are due to  $\text{CH}$  groups. Signals that appear as negative peaks in the DEPT  $135^\circ$  spectrum are due to  $\text{CH}_2$  groups, and signals that appear as positive peaks in the DEPT  $135^\circ$  spectrum but are absent from the DEPT  $90^\circ$  spectrum are due to  $\text{CH}_3$  groups. DEPT and broadband decoupled spectra of ethyl 2-propenoate are shown in Figure 14.12. With the use of computer addition and subtraction of spectra, many modern NMR spectrometers automatically report the results of a DEPT experiment as three spectra: one that shows only peaks due to  $\text{CH}_3$  groups, one that shows only peaks due to  $\text{CH}_2$  groups, and one that shows only peaks due to  $\text{CH}$  groups. When combined with the broadband decoupled spectrum, the number of hydrogens on each carbon is readily identified. The remaining  $^{13}\text{C}$ -NMR spectra in this book are broadband decoupled spectra with the information obtained from the DEPT spectra indicated above each peak as  $\text{C}$ ,  $\text{CH}$ ,  $\text{CH}_2$ , or  $\text{CH}_3$ .

As you examine more  $^{13}\text{C}$ -NMR spectra, you will find that the heights (which are proportional to the areas) of the peaks often do not directly correspond to the number of carbons responsible for those peaks. Factors other than the number of carbons also affect the areas of the peaks. Although it is possible to obtain an accurate integral experimentally, the process is time consuming and is not usually done.

In summary, considerable information is available from a  $^{13}\text{C}$ -NMR spectrum. First, the number of different carbons can be counted, providing information about the symmetry of the molecule. Second, the chemical environment of the carbons can be deduced from their chemical shifts. Third, information from the DEPT spectra tells how many hydrogens are bonded to each carbon. Some of this same information is provided by the  $^1\text{H}$ -NMR spectrum. However, the two types of spectra often provide complementary information and help solidify deductions made with one alone.  $^{13}\text{C}$ -NMR is especially useful when the  $^1\text{H}$ -NMR spectrum is too complex for ready interpretation.

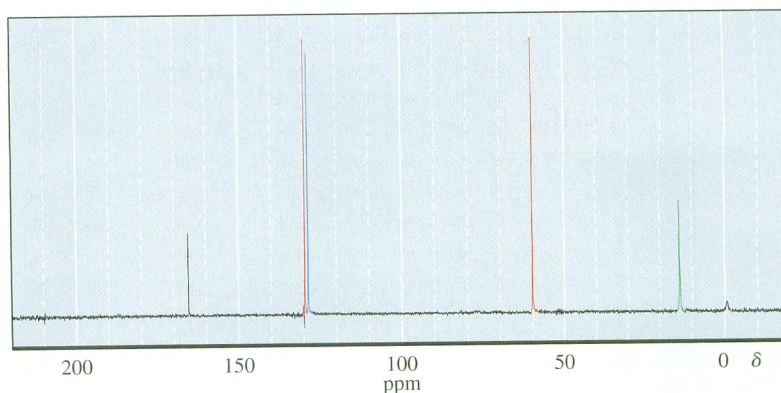
Let's look at some examples of structure determination using  $^{13}\text{C}$ -NMR spectroscopy. Figure 14.13 shows the spectrum of  $\text{C}_8\text{H}_{10}$ . First, calculation indicates that the DU is 4. The compound has some symmetry, because the spectrum shows the presence of only four different types of carbons. When there is symmetry, it is often useful to also count the number of hydrogens indicated by the spectrum, because this may tell us which signals are the result of more than one identical carbon in the compound. In this case the formula obtained by adding the fragments in the spectrum is  $\text{C}_4\text{H}_5$ . This accounts for half of the carbons and half of the hydrogens, suggesting that there are two carbons of each type. Examination of the chemical shifts shows one alkyl type and three alkene/aromatic types. A benzene ring is consistent with the DU of 4. The signal at  $19.5\ \delta$  is due to a methyl group. The signals at  $125.9$  and  $129.7\ \delta$  are due to carbons bonded to one hydrogen, and the signal at  $136.2\ \delta$  is due to a carbon that is not bonded to any hydrogens. If





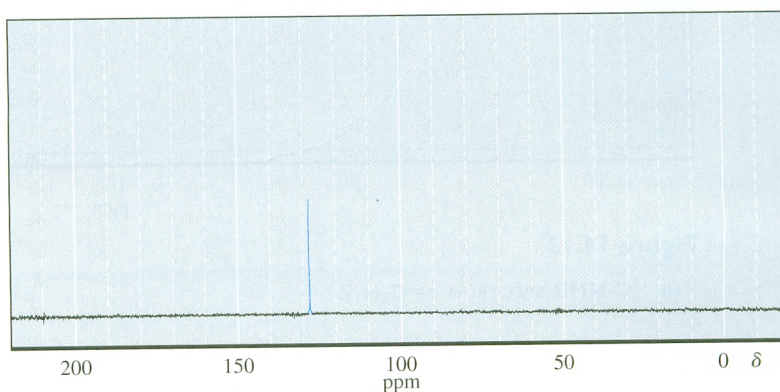
Ethyl 2-propenoate

Broadband decoupled spectrum



DEPT 90° spectrum

(Only the carbons of CH groups appear.)



DEPT 135° spectrum

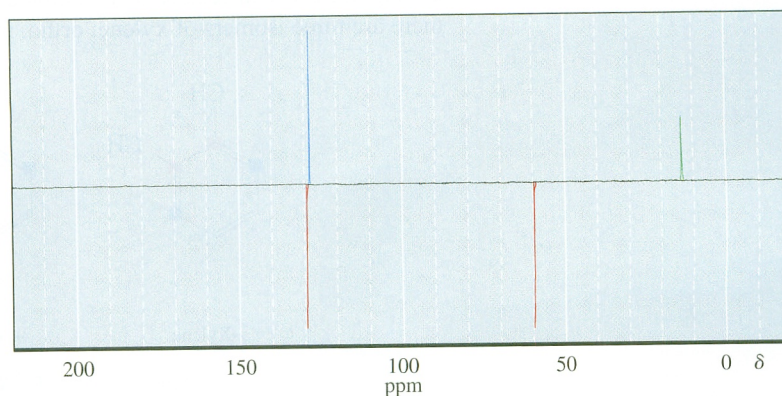
(The carbons of CH<sub>2</sub> groups appear as negative absorptions, whereas the carbons of CH and CH<sub>3</sub> groups appear as positive absorptions.)

Figure 14.12

**BROADBAND DECOUPLED AND DEPT <sup>13</sup>C-NMR SPECTRA OF ETHYL 2-PROPENOATE.** The peaks are assigned as follows: the peak at 166 δ is due to a C with no attached H's (C-1) because it appears only in the broadband decoupled spectrum; the peak at 129.7 δ is due to an alkene CH<sub>2</sub> (C-3) because it appears as a negative peak in the DEPT 135° spectrum; the peak at 128.7 δ is due to an alkene CH (C-2) because it appears in the DEPT 90° spectrum; the peak at 60 δ is due to a CH<sub>2</sub> (C-4) because it appears as a negative peak in the DEPT 135° spectrum; and the peak at 14 δ is due to a CH<sub>3</sub> (C-5) because it appears as a positive peak in the DEPT 135° spectrum but does not appear in the DEPT 90° spectrum.



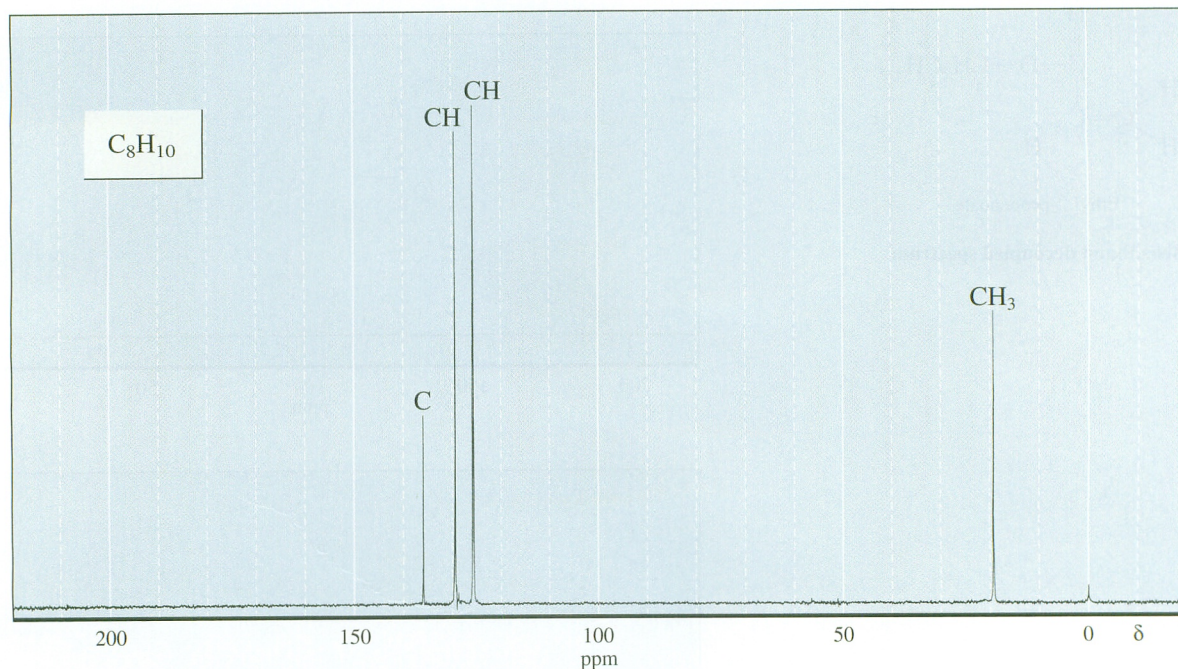
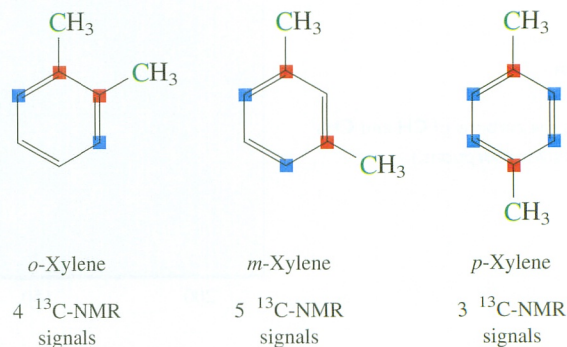


Figure 14.13

THE  $^{13}\text{C}$ -NMR SPECTRUM OF  $\text{C}_8\text{H}_{10}$ .

there are indeed two of each of these types of carbons, then the fragments 2  $\text{CH}_3$ , 2  $\text{CH}$ , 2  $\text{CH}$ , and 2  $\text{C}$  can readily be assembled to form dimethylbenzene (xylene). However, there are three isomers of xylene: *ortho*, *meta*, and *para*.



These isomers can be distinguished on the basis of their  $^{13}\text{C}$ -NMR spectra because they have different symmetries. The *ortho*-isomer has four different carbons, the *meta*-isomer has five, and the *para*-isomer has only three. The unknown must be *ortho*-xylene. Note that this compound could be identified as one of the xylene isomers on the basis of its  $^1\text{H}$ -NMR spectrum, but it would be difficult to establish which isomer it is from just that information.

As another example, consider the spectrum of  $\text{C}_6\text{H}_{12}\text{O}$ , shown in Figure 14.14. The DU is 1. Examination of the  $^{13}\text{C}$ -NMR spectrum shows five different types of carbons.



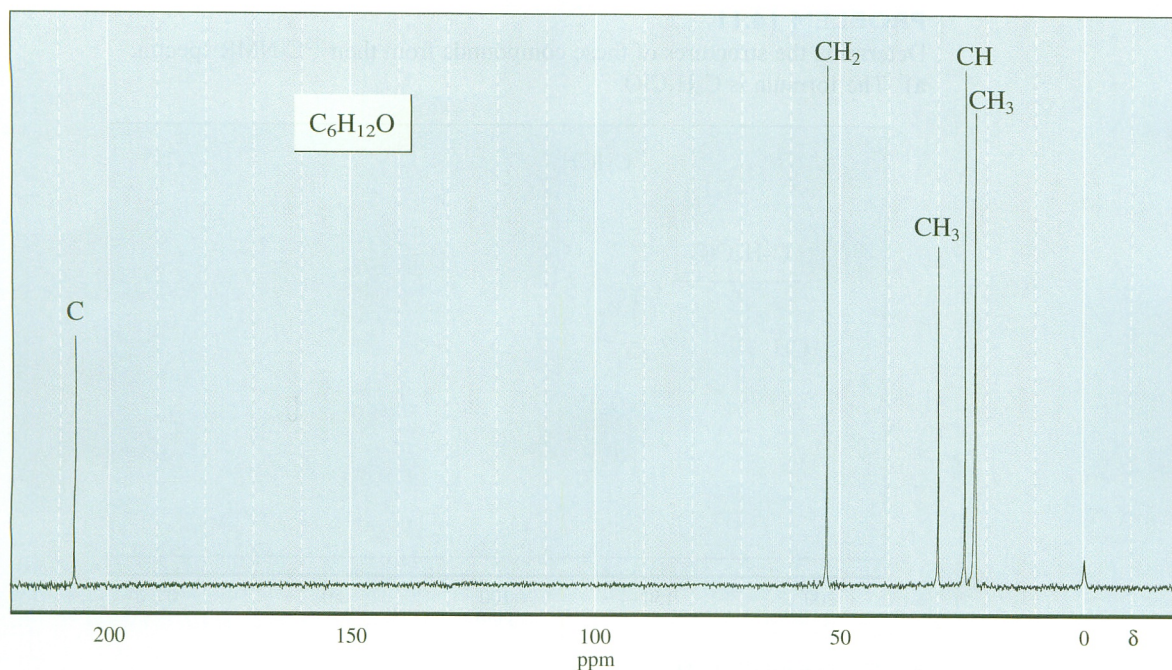
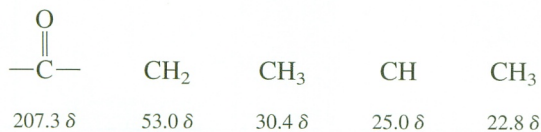


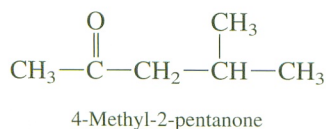
Figure 14.14

THE  $^{13}\text{C}$ -NMR SPECTRUM OF  $\text{C}_6\text{H}_{12}\text{O}$ .

Therefore, there must be two carbons that appear at identical chemical shifts because they are chemically equivalent. The spectrum accounts for only nine hydrogens, so the extra carbon is probably a  $\text{CH}_3$  group that is identical to one of the other  $\text{CH}_3$  groups. (However, remember that OH and NH hydrogens will not appear in the  $^{13}\text{C}$ -NMR spectrum.) The peak at 207.3  $\delta$  is due to a carbonyl carbon. (This accounts for the one degree of unsaturation.) It has no hydrogens bonded to it, so it is bonded to two carbons—the unknown is a ketone. From the remaining peaks in the spectrum the following fragments can be deduced:



These fragments total to  $\text{C}_5\text{H}_9\text{O}$ , so there must indeed be an additional  $\text{CH}_3$  group to account for the actual formula of  $\text{C}_6\text{H}_{12}\text{O}$ . The two alkyl carbons that appear farthest downfield, the  $\text{CH}_2$  at 53.0  $\delta$  and the  $\text{CH}_3$  at 30.4  $\delta$ , are probably bonded to the electronegative carbonyl group. By putting the remaining fragments together, we see that the compound is 4-methyl-2-pentanone. The two methyl groups of the isobutyl group are chemically equivalent, and both appear at 22.8  $\delta$ .

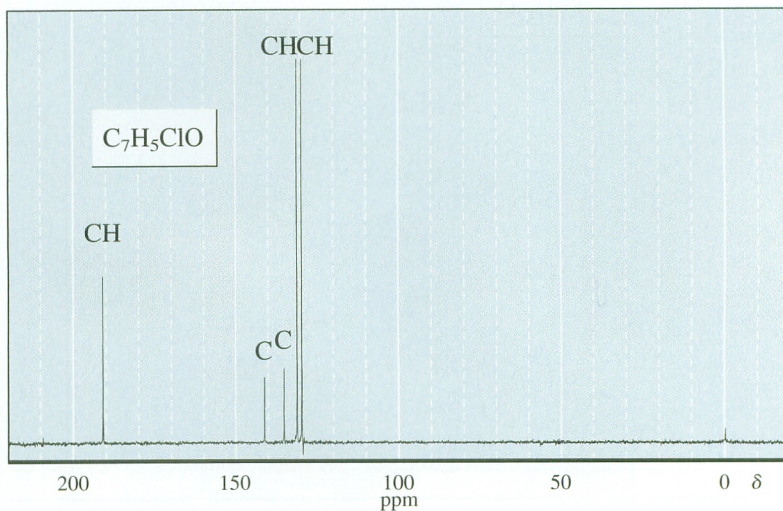




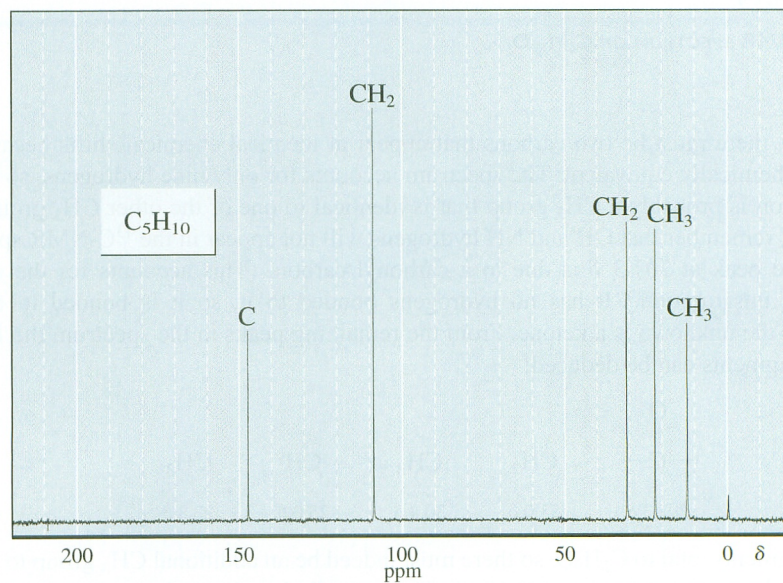
**PROBLEM 14.11**

Determine the structures of these compounds from their  $^{13}\text{C}$ -NMR spectra:

a) The formula is  $\text{C}_7\text{H}_5\text{ClO}$ .

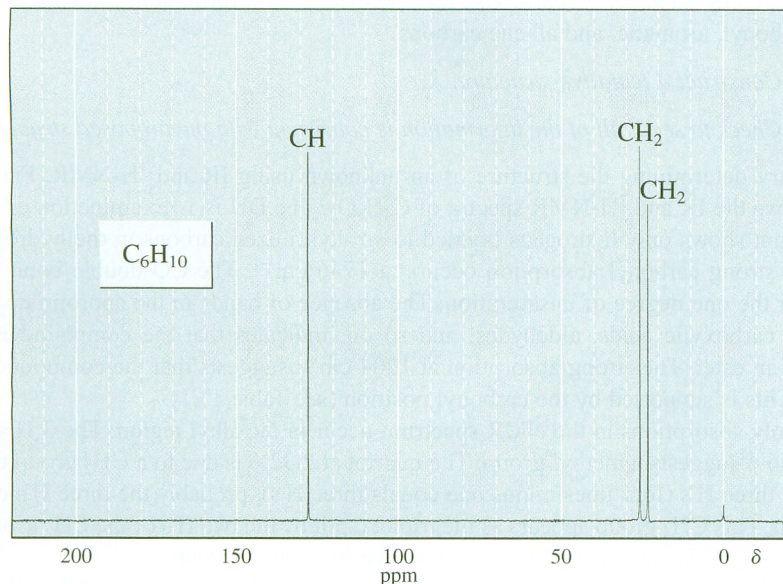


b) The formula is  $\text{C}_5\text{H}_{10}$ .





c) The formula is  $C_6H_{10}$ .



## 14.10 SOLVED PROBLEMS EMPLOYING IR AND NMR SPECTRA

Most structure determination problems that are encountered in real-life situations in the laboratory rely on a combination of these spectral methods for solution. A general strategy that is often successful is as follows:

- Step 1.** Calculate the degree of unsaturation if the formula is available.
- Step 2.** Examine the IR spectrum to determine the functional group. Do not forget the information provided by the formula. For example, a compound with only one oxygen cannot be a carboxylic acid, nor can a compound with a DU of 3 contain a benzene ring. Some structural features suggested by the IR spectrum can be rapidly confirmed by examination of the  $^1H$ -NMR spectrum. For example, it is often difficult to be confident of the presence of an aromatic ring based solely on examination of the IR spectrum. However, hydrogens on a benzene ring appear in a characteristic region of the NMR spectrum. Likewise, the H of an aldehyde group and the H of a carboxylic acid can be readily identified in the NMR spectrum.
- Step 3.** Examine the  $^1H$ -NMR spectrum as described on pages 566–567. Examine the general positions of the peaks. Examine the integral for the ratios of the different kinds of hydrogens. Examine the coupling patterns. Remember that the number of nearby hydrogens coupled to the hydrogen(s) being examined is one less than the number of peaks.



**Step 4.** *Examine the  $^{13}\text{C}$ -NMR spectrum.* Count the number of peaks to see if there are any identical carbons. Use the chemical shift information to identify carbonyl, aromatic, and alkene carbons.

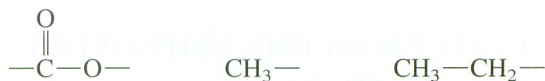
**Step 5.** *Construct a tentative structure.*

**Step 6.** *Check to see if all of the information is consistent with the proposed structure.*

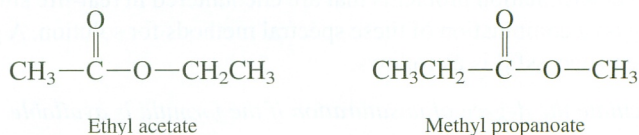
Let's try determining the structure of an unknown using IR and  $^1\text{H}$ -NMR. Figure 14.15 shows the IR and  $^1\text{H}$ -NMR spectra of  $\text{C}_4\text{H}_8\text{O}_2$ . The DU is 1. Examination of the IR spectrum shows only hydrogens bonded to  $sp^3$ -hybridized carbons in the hydrogen region. A strong carbonyl absorption occurs at  $1746\text{ cm}^{-1}$ . The CO double bond accounts for the one degree of unsaturation. The absence of bands in the appropriate regions for carboxylic acids, aldehydes, and so on, indicates that the compound is a ketone or an ester. The strong absorption at  $1204\text{ cm}^{-1}$  suggests that the compound is an ester. This is supported by the carbonyl position (see Table 13.1).

The only absorptions in the NMR spectrum occur in the alkyl region. The 3 H singlet at  $3.66\text{ }\delta$  suggests a methyl group. The quartet at  $2.32\text{ }\delta$  is due to a  $\text{CH}_2$  group that is split by three H's (four lines minus one equals three H's), probably the three H's of a  $\text{CH}_3$  group. This  $\text{CH}_3$  group appears as the triplet (split by the two H's of the  $\text{CH}_2$  group) at  $1.12\text{ }\delta$ . These two signals indicate the presence of an ethyl group.

On the basis of the IR and the NMR spectra the following fragments are known to be present:



Two possible esters can be assembled from these fragments:



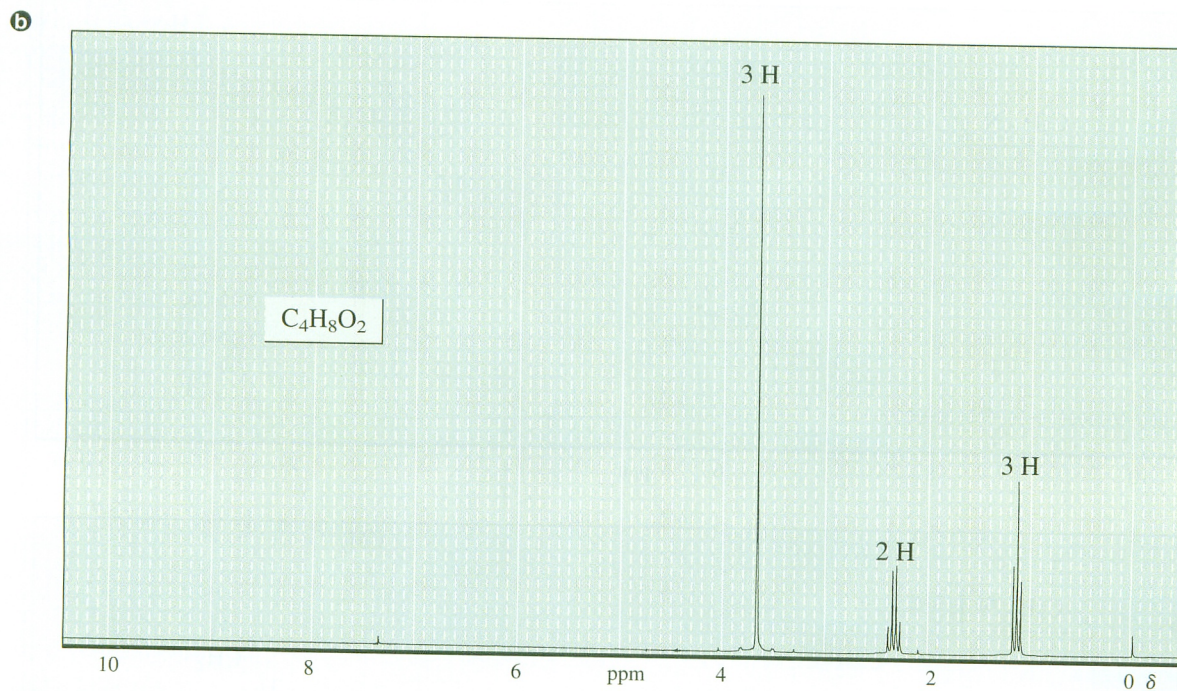
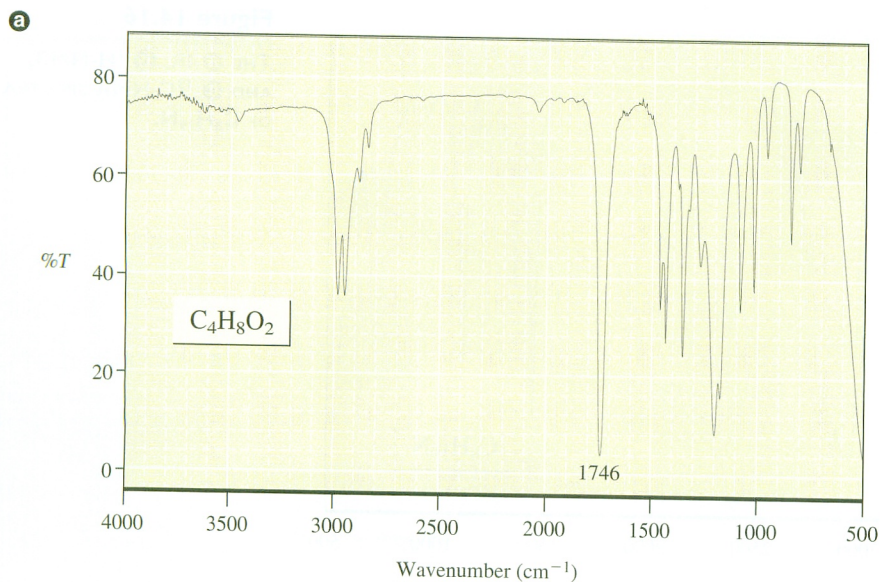
These esters can be readily distinguished on the basis of chemical shifts. On the basis of Table 14.1, the methyl group attached to the carbonyl of ethyl acetate is predicted to appear near  $2.0\text{ }\delta$ , and the  $\text{CH}_2$  of the ethyl group should appear slightly downfield from  $3.7\text{ }\delta$ . For methyl propanoate the predictions are  $3.7\text{ }\delta$  for the methyl group attached directly to the oxygen of the ester and slightly downfield from  $2.0\text{ }\delta$  for the  $\text{CH}_2$  bonded to the carbonyl group. In other words, because the signal for the  $\text{CH}_3$  is further downfield than the signal for the  $\text{CH}_2$  of the ethyl group, the  $\text{CH}_3$  must be bonded to the oxygen. The compound is methyl propanoate.

Let's now try an example using IR and both types of NMR. Figure 14.16 shows the IR,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR spectra for  $\text{C}_8\text{H}_{19}\text{N}$ . The DU for this compound is zero, so it has no pi bonds or rings. On the basis of the presence of nitrogen and  $\text{DU} = 0$ , the unknown must be an amine. The absorption bands from  $3000$  to  $2800\text{ cm}^{-1}$  in the IR spectrum show hydrogens bonded to  $sp^3$ -hybridized carbons, as expected. The small absorption at  $3280\text{ cm}^{-1}$  suggests that the compound is a secondary amine, although caution must be exercised when assigning a weak band such as this one.

In the  $^1\text{H}$ -NMR spectrum the peak at  $2.61\text{ }\delta$  can be recognized as a distorted triplet. This suggests that the hydrogens that are responsible for this signal are near two hydrogens, but the coupling is beginning to deviate from first order. The complex multi-



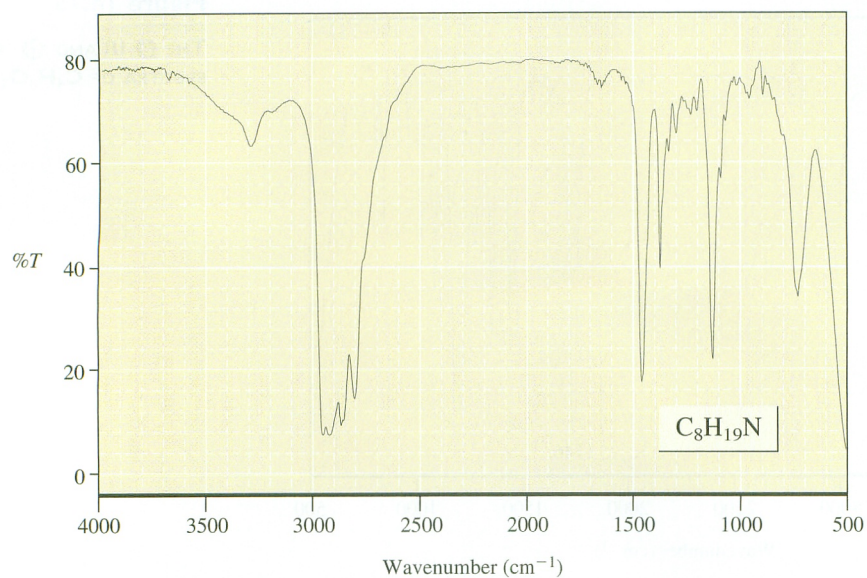
Figure 14.15

THE **a** IR AND **b**  $^1\text{H}$ -NMR SPECTRA OF  $\text{C}_4\text{H}_8\text{O}_2$ .

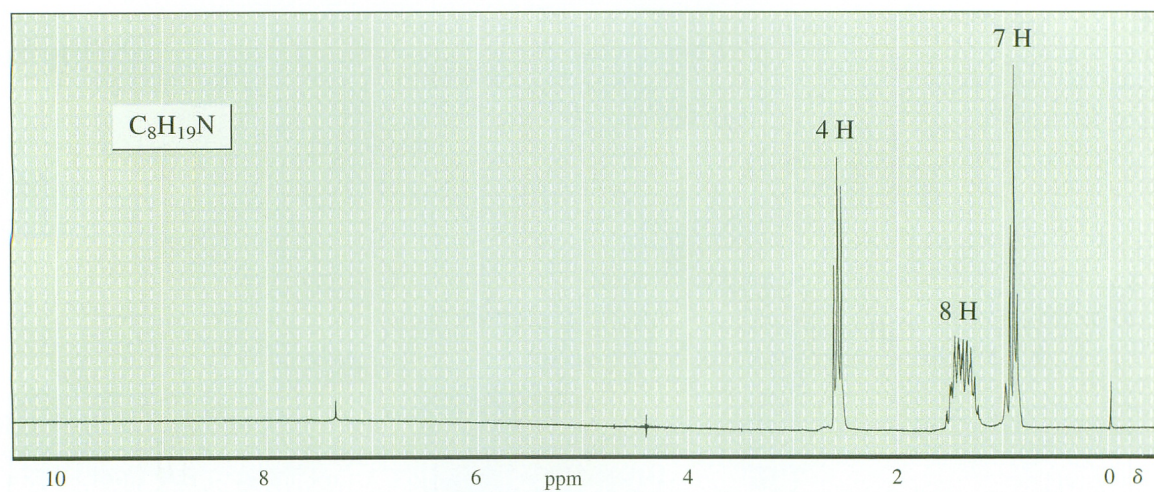
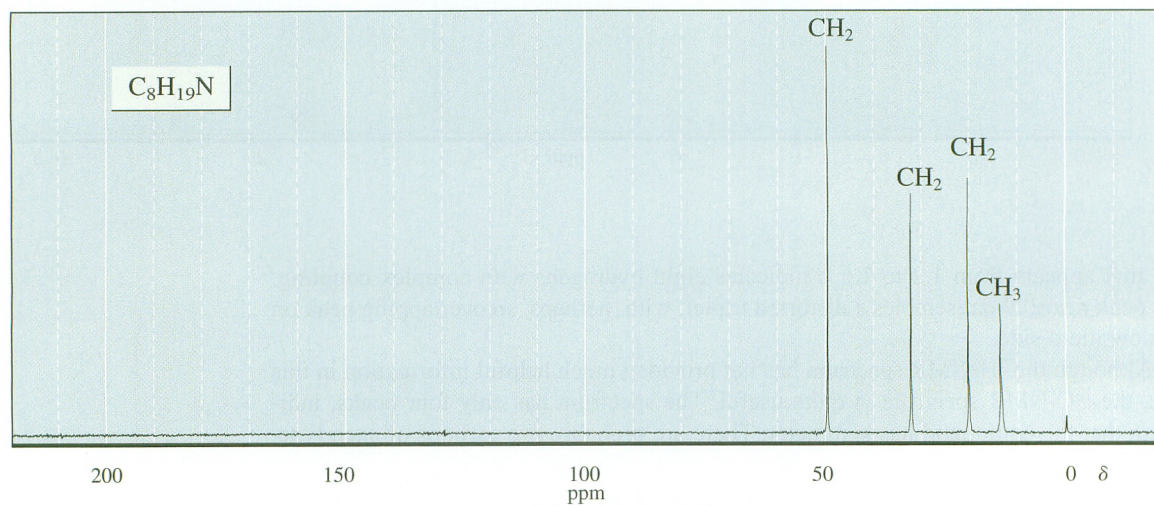
plet that appears from 1.2 to 1.6  $\delta$  indicates eight hydrogens with complex coupling. The peak near 0.9  $\delta$  resembles a distorted triplet, with, perhaps, an overlapping peak on the downfield side.

Although the  $^1\text{H}$ -NMR spectrum has not provided much helpful information in this case, the  $^{13}\text{C}$ -NMR spectrum is quite useful. The spectrum has only four peaks, indicating that the compound has symmetry. There are probably two carbons of each type.



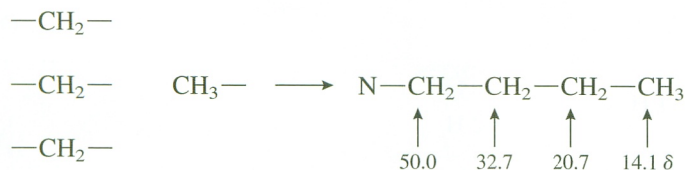
**a****Figure 14.16**

THE **a** IR, **b**  $^1H$ -NMR, AND **c**  $^{13}C$ -NMR SPECTRA OF  $C_8H_{19}N$ .

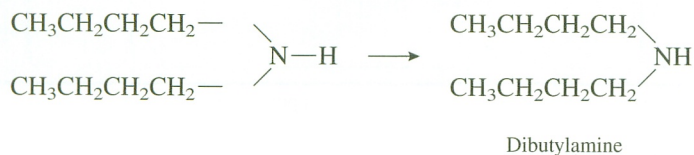
**b****c**



There are three  $\text{CH}_2$  groups and one  $\text{CH}_3$  group. These fragments can be assembled only into a butyl group. This group is attached to a nitrogen. The carbons closer to the nitrogen are shifted farther downfield:



On the basis of the symmetry of the molecule, it must have two chemically equivalent butyl groups. This accounts for 18 hydrogens. The 19th hydrogen must be bonded to the nitrogen (recall the NH absorption in the IR spectrum). These fragments can now be assembled to produce dibutylamine:



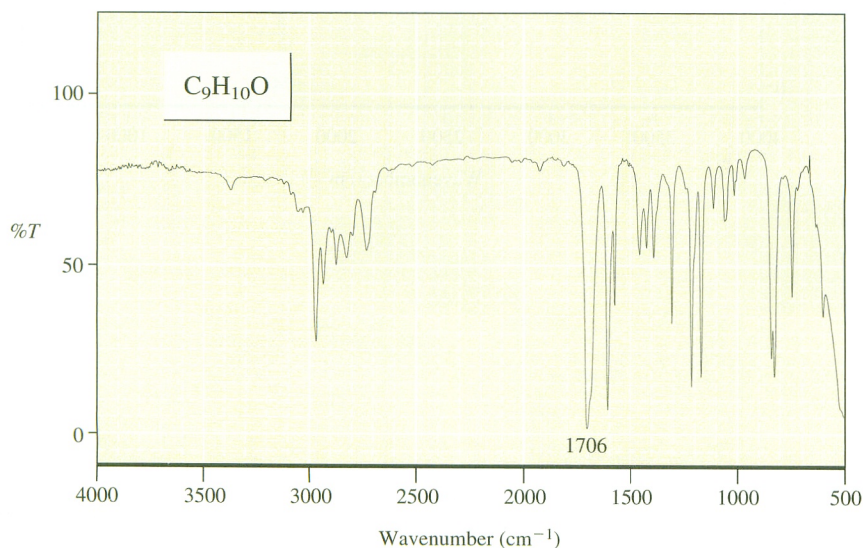
At this point we should check to make certain that this structure is consistent with the chemical shifts and coupling in the  $^1\text{H}$ -NMR spectrum. Note that the H on the N is responsible for the peak near 1  $\delta$  on the downfield side of the distorted triplet.

This chapter has provided some examples and general guidelines for the use of IR and NMR spectra to solve structure problems. However, each problem is unique, and the exact procedure will vary from problem to problem. The best way to become adept at using these techniques is to work as many problems as possible.

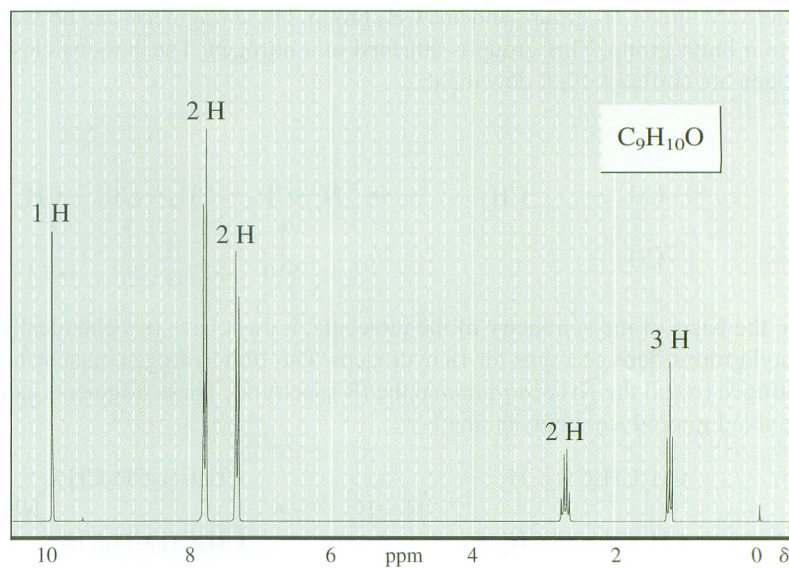
### PROBLEM 14.12

Determine the structures of these compounds from their IR and  $^1\text{H}$ -NMR spectra:

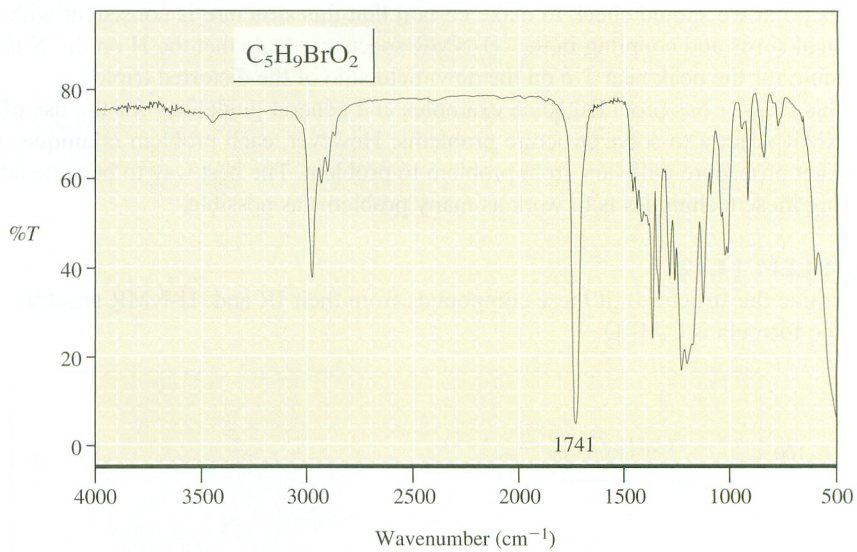
a) The formula is  $\text{C}_9\text{H}_{10}\text{O}$ .



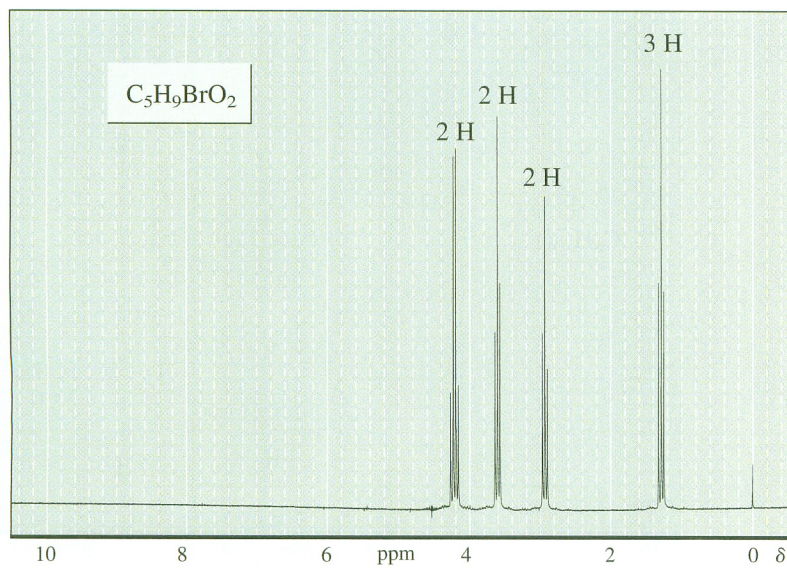




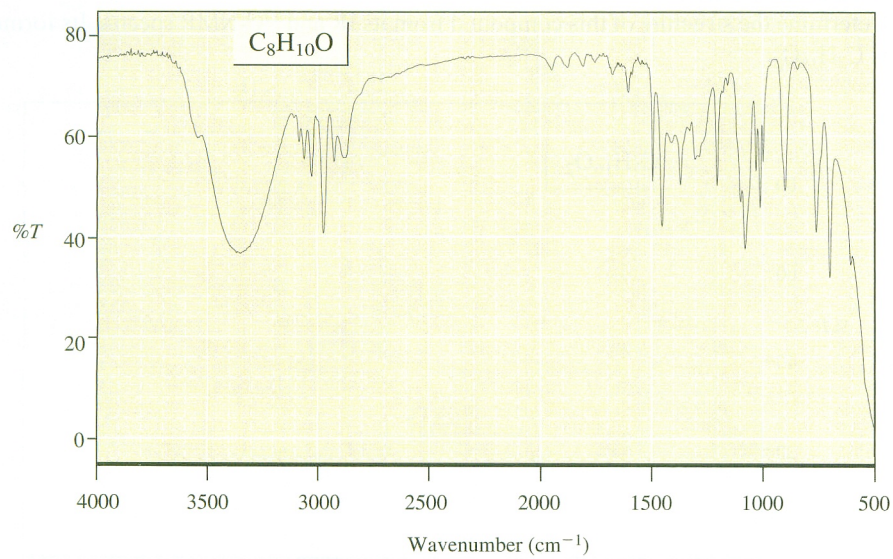
b) The formula is  $C_5H_9BrO_2$ .



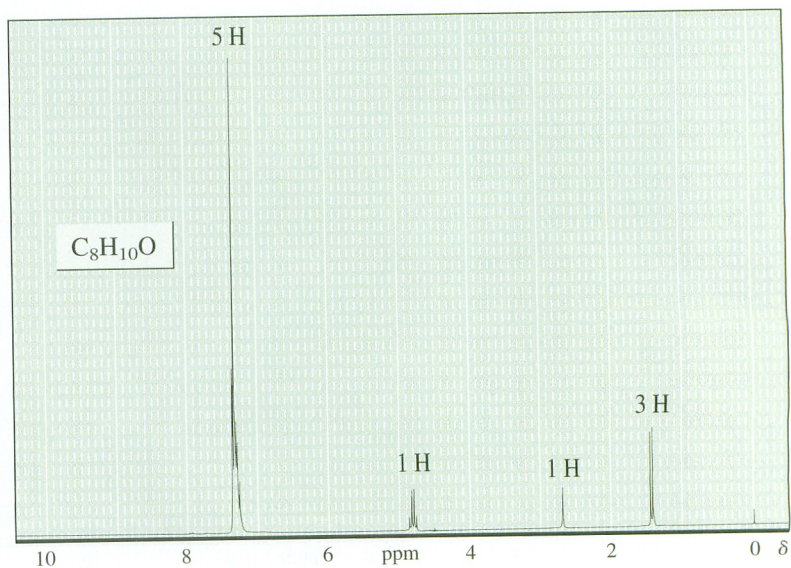




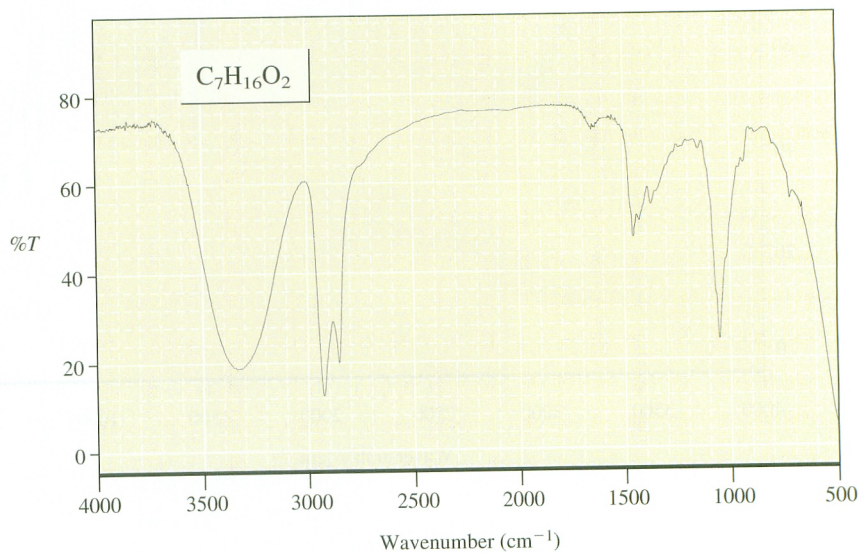
c) The formula is  $C_8H_{10}O$ .



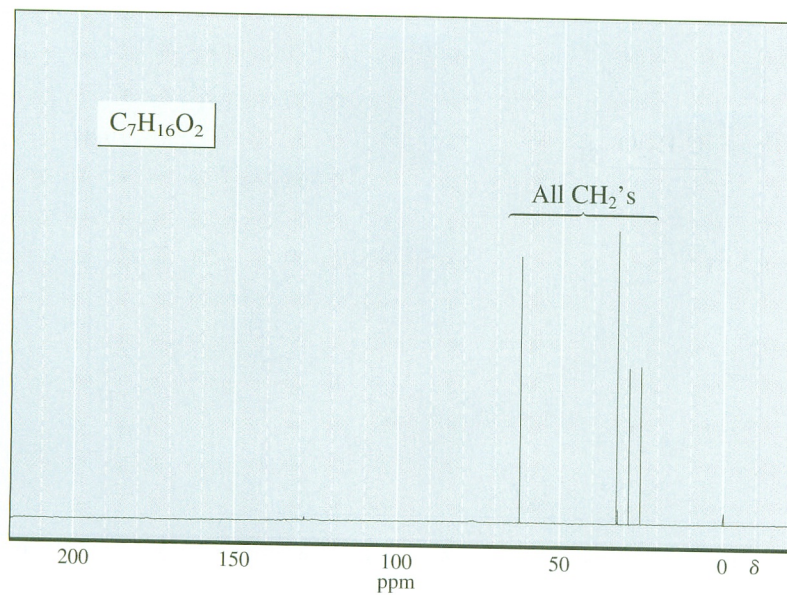


**PROBLEM 14.13**

Determine the structure of this compound from its IR and  $^{13}C$ -NMR spectra. Its formula is  $C_7H_{16}O_2$ :

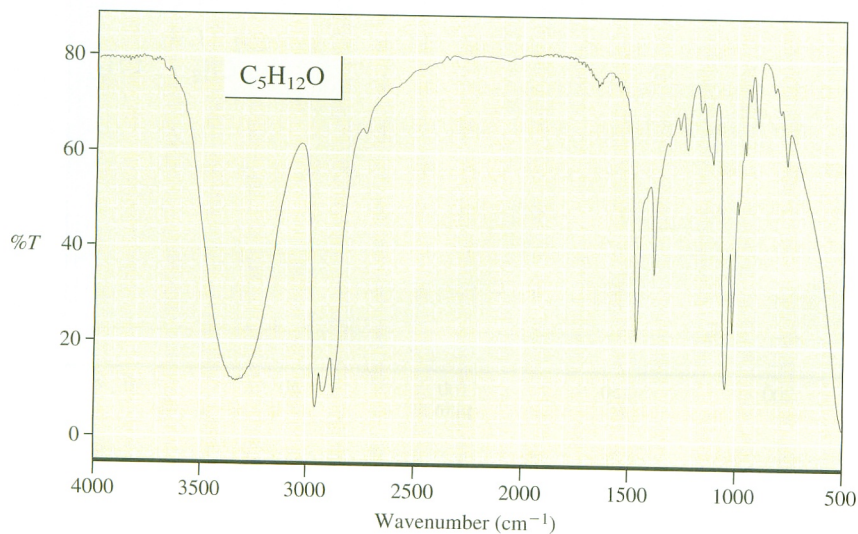




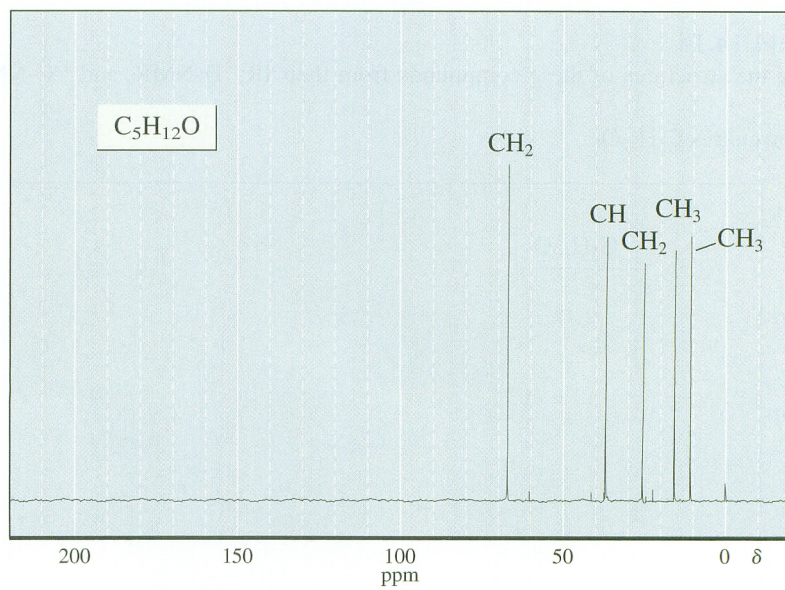
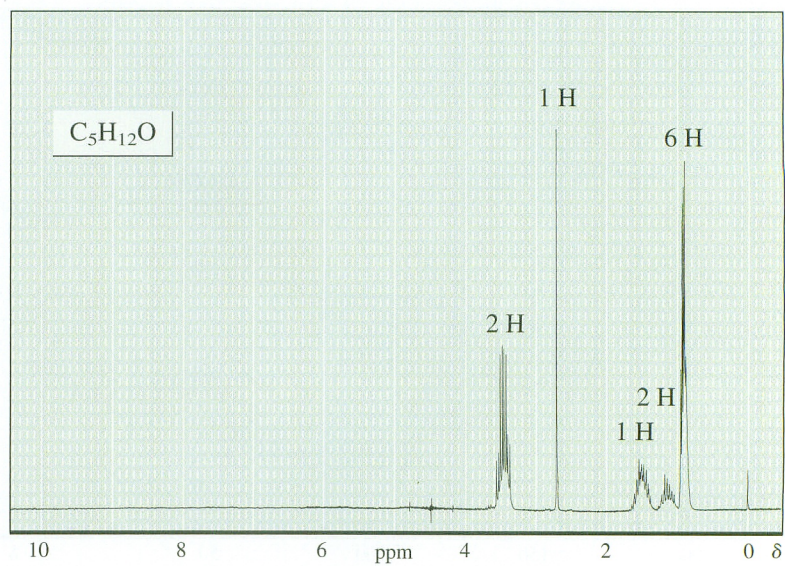
**PROBLEM 14.14**

Determine the structures of these compounds from their IR,  $^1H$ -NMR, and  $^{13}C$ -NMR spectra:

a) The formula is  $C_5H_{12}O$ .

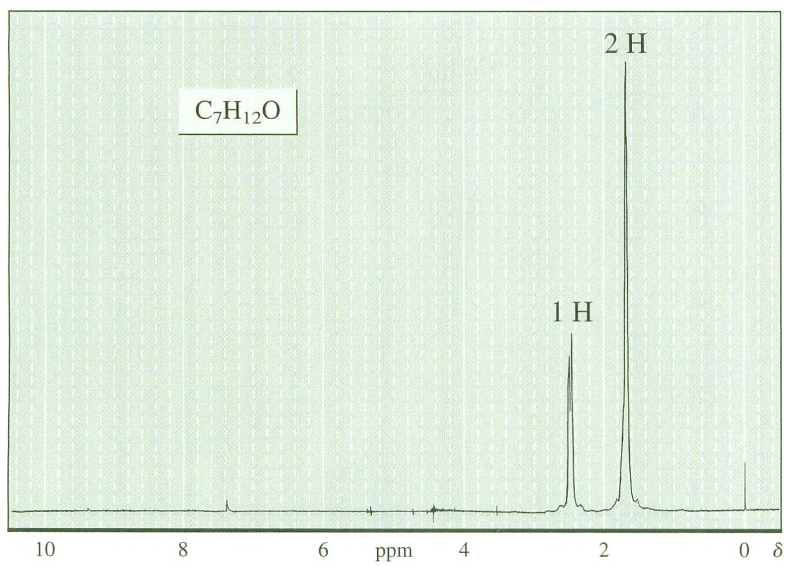
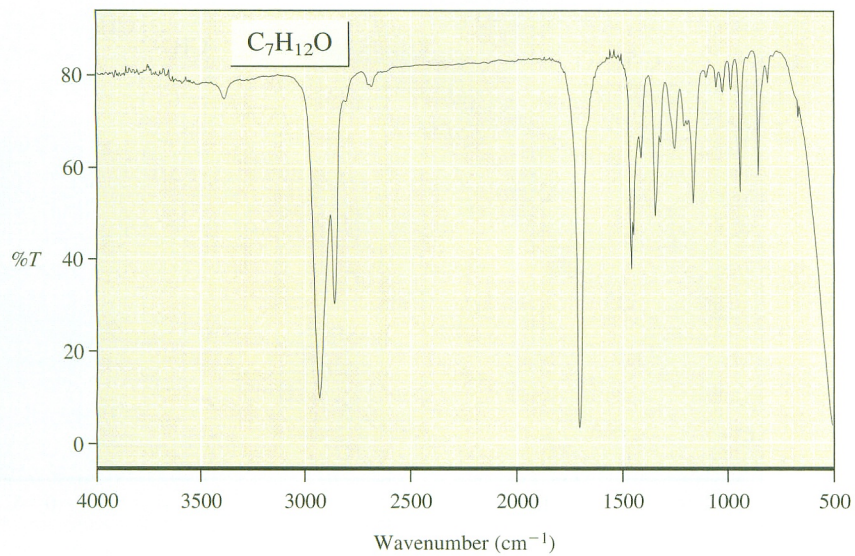




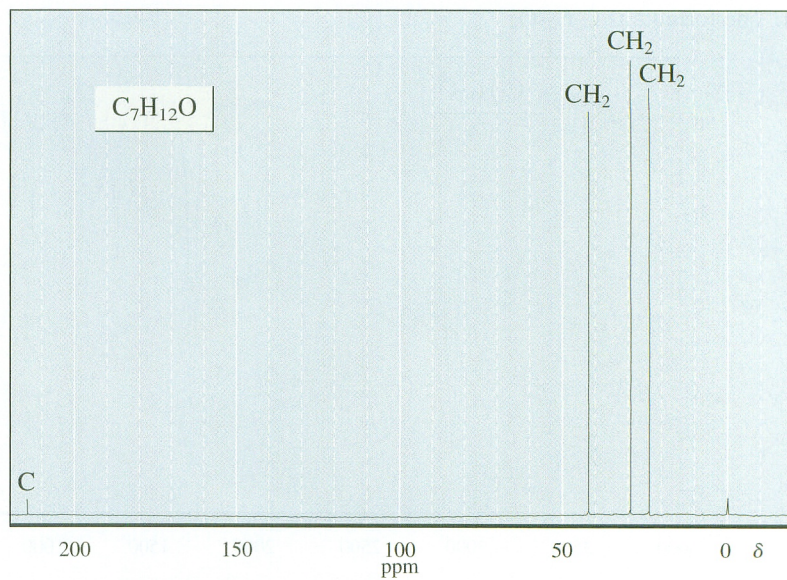




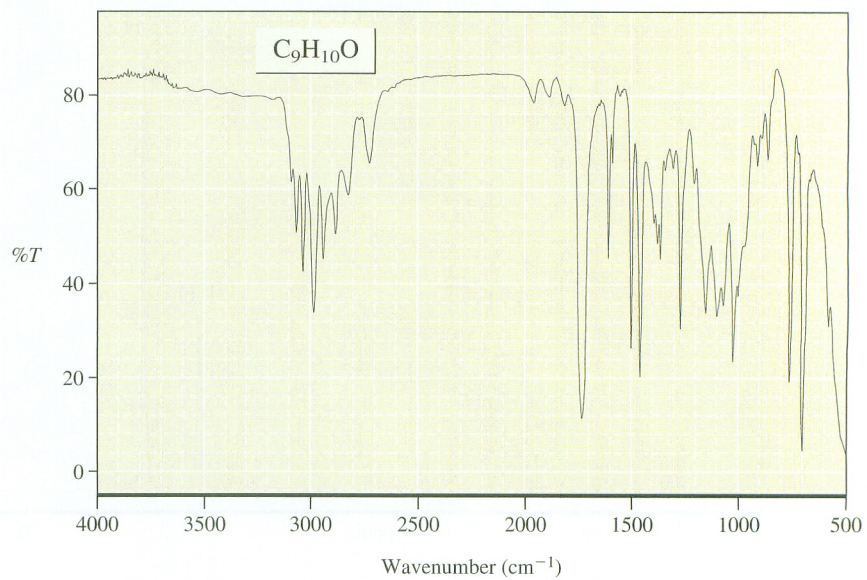
b) The formula is  $C_7H_{12}O$ .



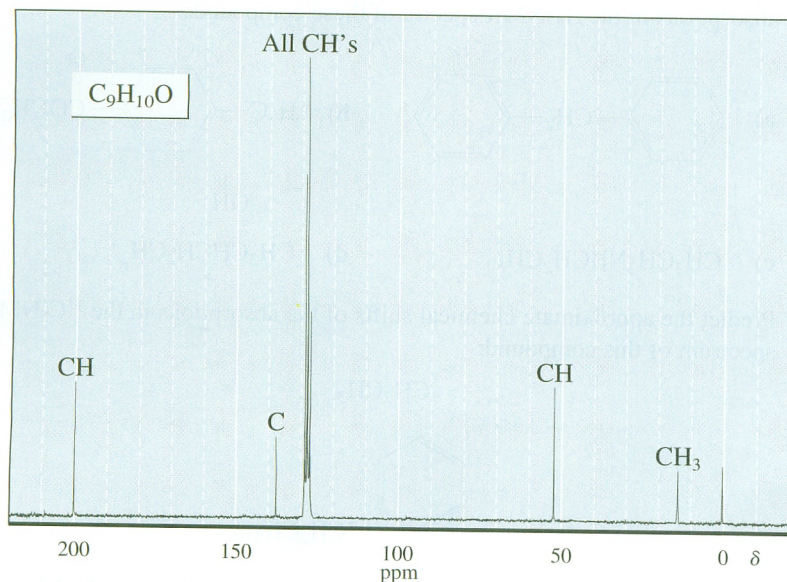
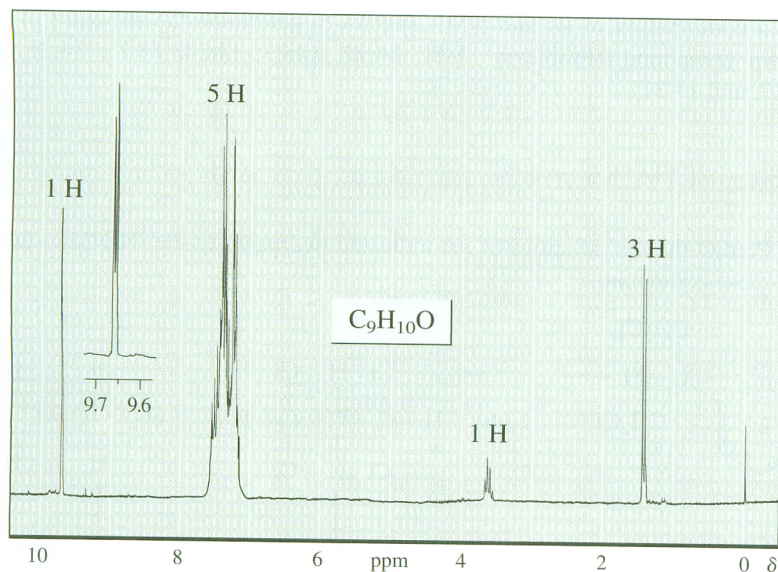




c) The formula is  $C_9H_{10}O$ .







## Review of Mastery Goals

*After completing this chapter, you should be able to:*

- Predict the approximate chemical shifts, multiplicity, and integrals of peaks in the  $^1\text{H}$ -NMR spectrum of a compound. (Problems 14.15, 14.16, 14.30, and 14.32)
- Predict the number and approximate chemical shifts of peaks in the  $^{13}\text{C}$ -NMR spectrum of a compound. (Problems 14.17 and 14.33)
- Determine the hydrocarbon skeleton of a compound by examination of its  $^1\text{H}$  and/or  $^{13}\text{C}$ -NMR spectrum. (Problems 14.18, 14.19, 14.20, and 14.28)

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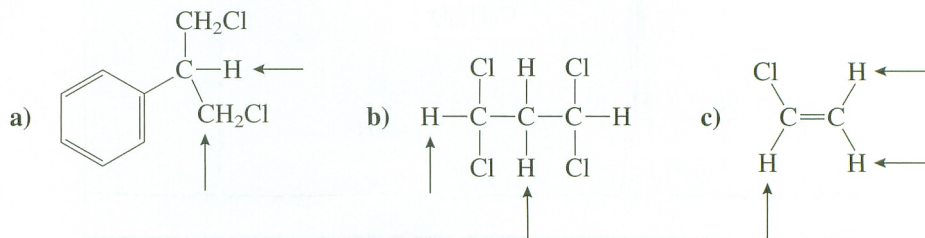


- Use a combination of IR and NMR spectra to determine the structure of an unknown compound. (Problems 14.21, 14.22, 14.23, 14.24, 14.25, 14.26, 14.27, 14.29, and 14.31)

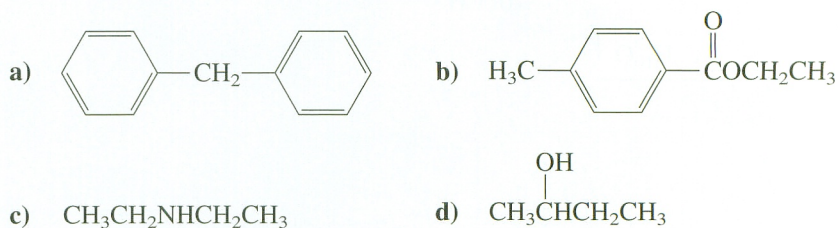
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## Additional Problems

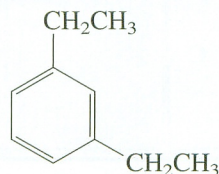
- 14.15** Predict the multiplicities of the indicated hydrogens in the  $^1\text{H}$ -NMR spectra of these compounds:



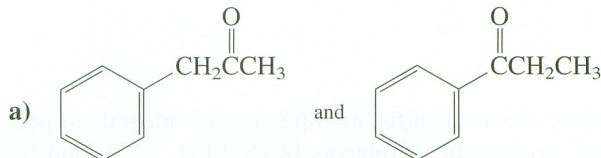
- 14.16** Predict the approximate chemical shifts, multiplicities, and integrals for the absorptions in the  $^1\text{H}$ -NMR spectra of these compounds:



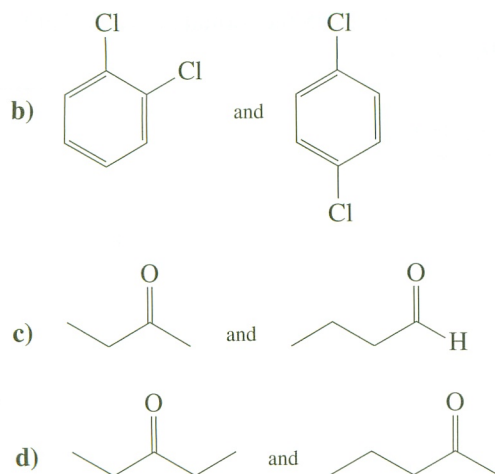
- 14.17** Predict the approximate chemical shifts of the absorptions in the  $^{13}\text{C}$ -NMR spectrum of this compound:



- 14.18** Suggest how these compounds could be distinguished by using NMR spectroscopy:



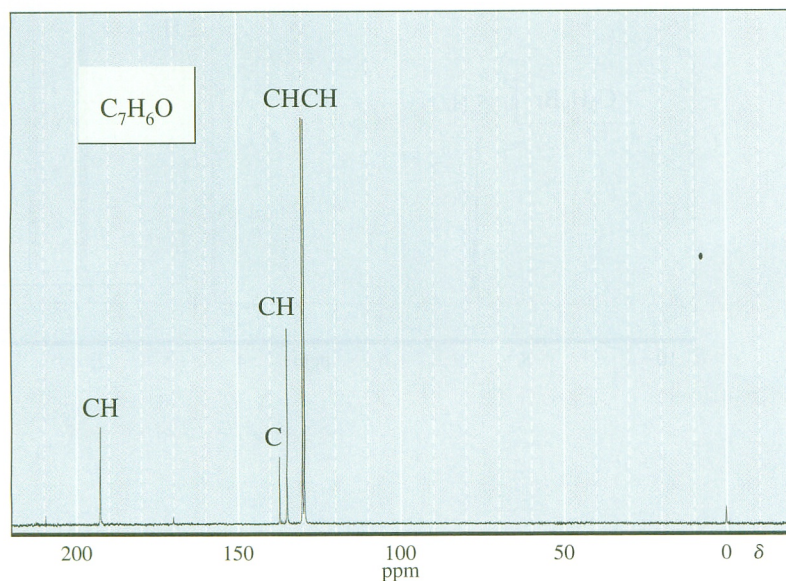




**14.19** Suggest structures for these compounds. First the formula is given. Then the absorptions in the  $^1\text{H-NMR}$  are listed as chemical shift (multiplicity, integral). Some compounds also have an important IR peak given.

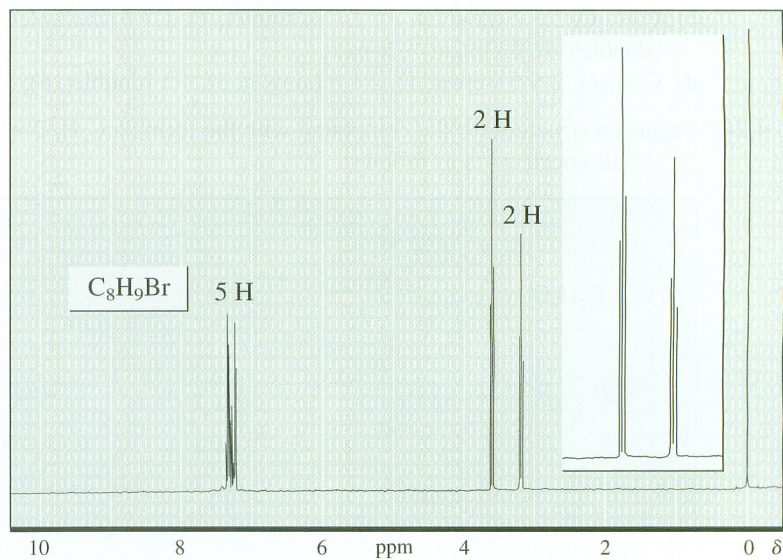
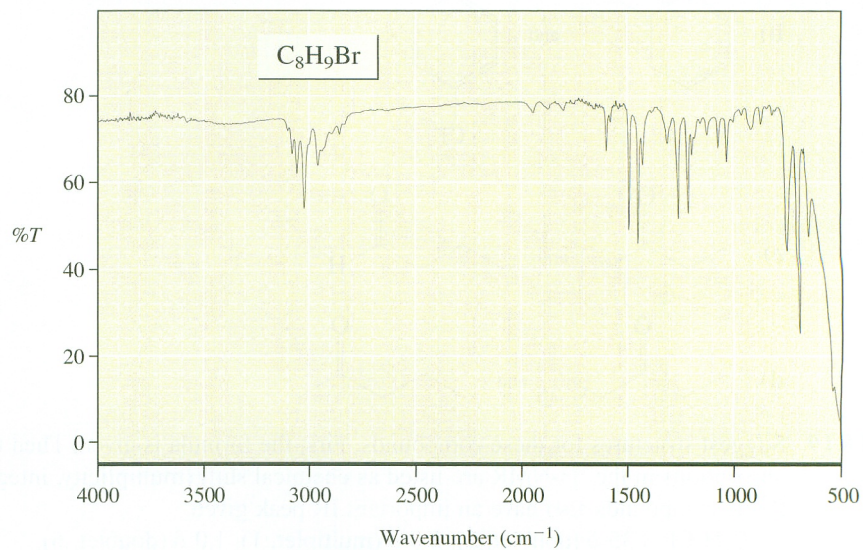
- a)  $\text{C}_4\text{H}_9\text{Cl}$ ; 3.35  $\delta$  (doublet, 2), 2.0  $\delta$  (multiplet, 1), 1.0  $\delta$  (doublet, 6).  
 b)  $\text{C}_3\text{H}_6\text{Br}_2$ ; 3.6  $\delta$  (triplet, 2), 2.4  $\delta$  (quintuplet, 1).  
 c)  $\text{C}_4\text{H}_{10}\text{O}$ ; 3.3  $\delta$  (doublet, 2), 2.4  $\delta$  (singlet, 1), 1.7  $\delta$  (multiplet, 1), 0.9  $\delta$  (doublet, 6); 3330  $\text{cm}^{-1}$ , broad.  
 d)  $\text{C}_5\text{H}_{10}\text{O}$ ; 2.6  $\delta$  (septet, 1), 2.1  $\delta$  (singlet, 3), 1.1 (doublet, 6); 1716  $\text{cm}^{-1}$ .

**14.20** Suggest a structure for the compound with the formula  $\text{C}_7\text{H}_6\text{O}$  whose  $^{13}\text{C-NMR}$  spectrum is as follows:



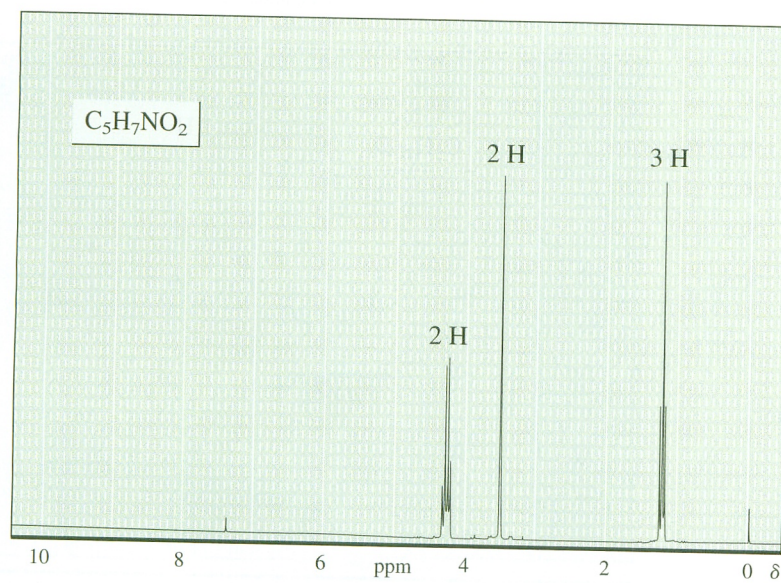
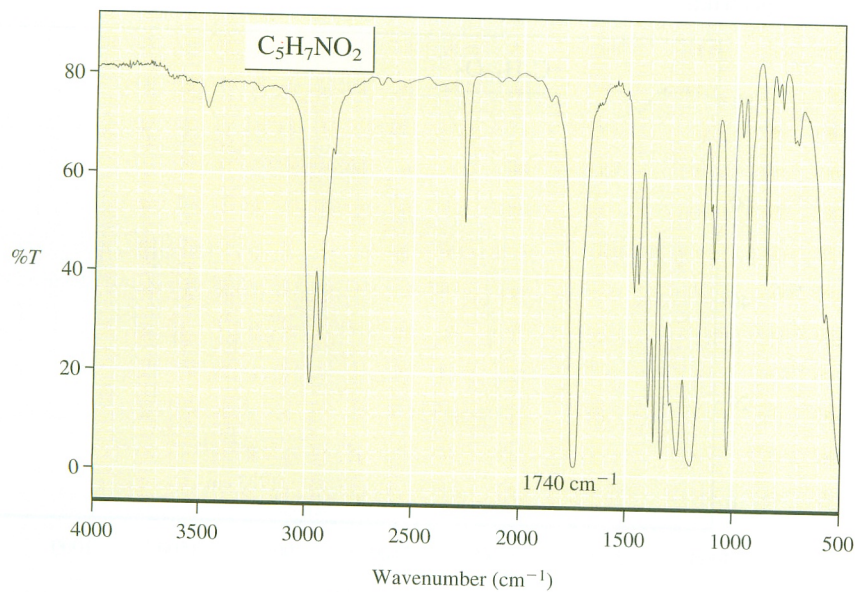


**14.21** Suggest a structure for the compound with the formula  $C_8H_9Br$  that has the following IR and  $^1H$ -NMR spectra:



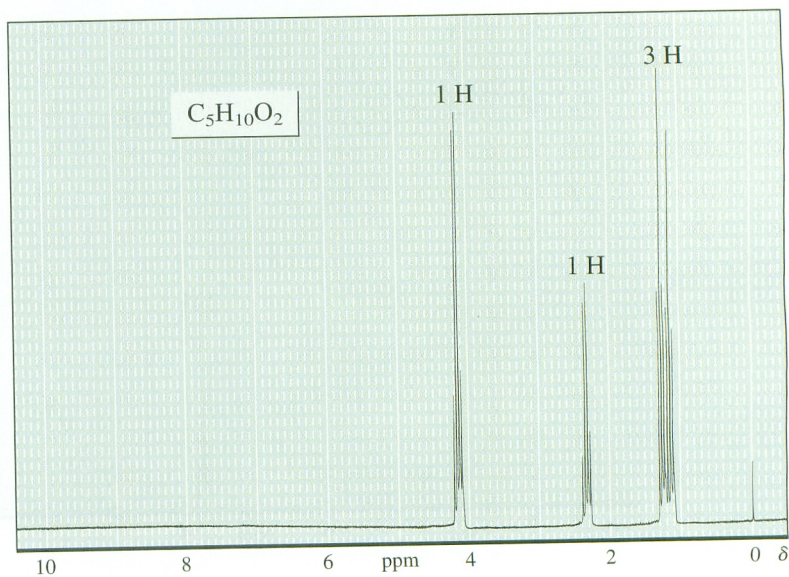
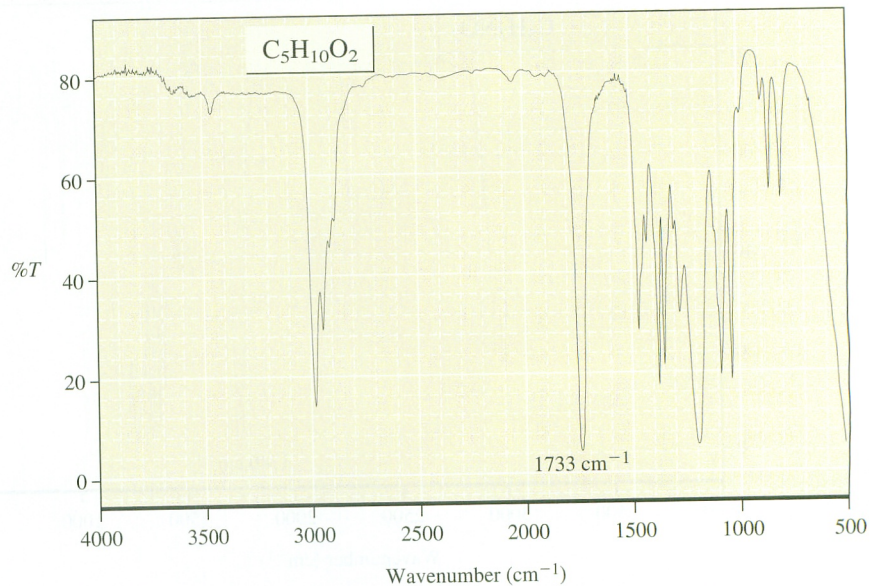


- 14.22 Suggest a structure for the compound with the formula  $C_5H_7NO_2$  that has the following IR and  $^1H$ -NMR spectra:



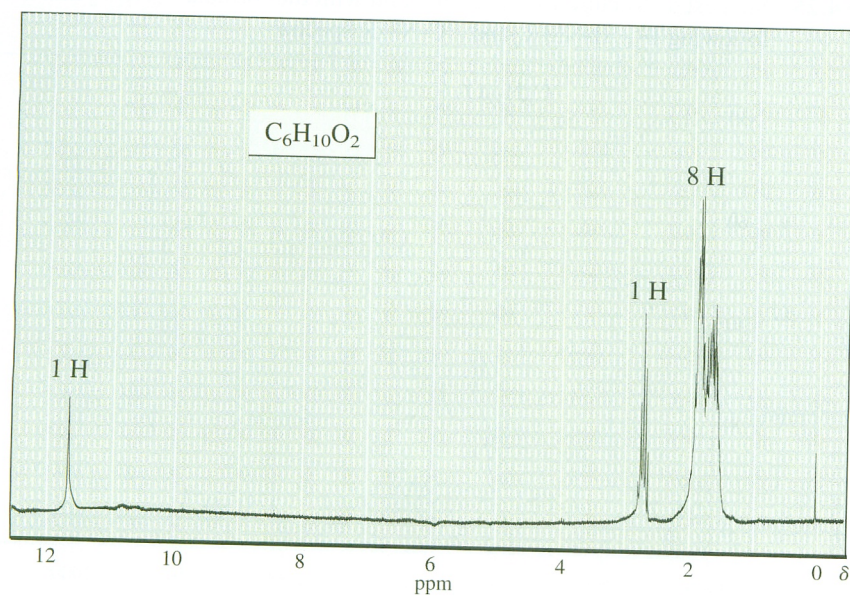
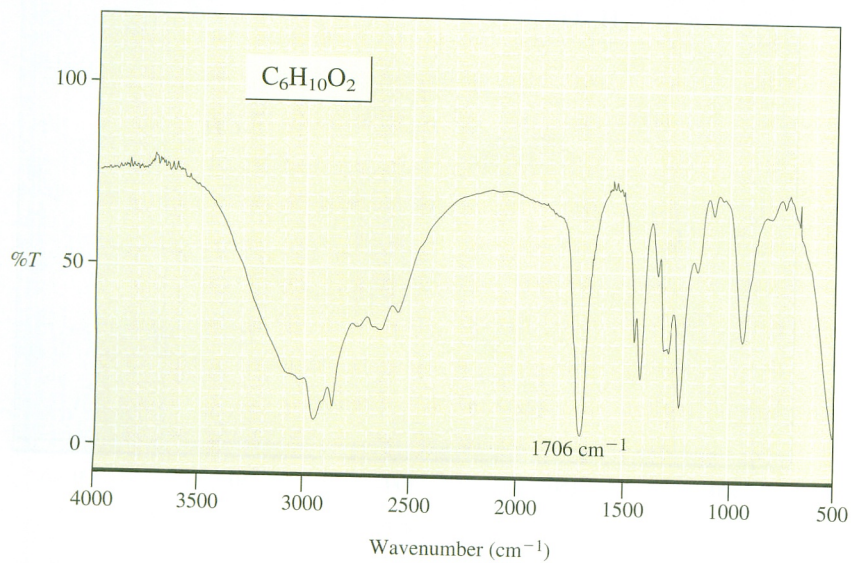


- 14.23** Suggest a structure for the compound with the formula  $C_5H_{10}O_2$  that has the following IR and  $^1H$ -NMR spectra. (Some absorptions overlap in the NMR spectrum.)

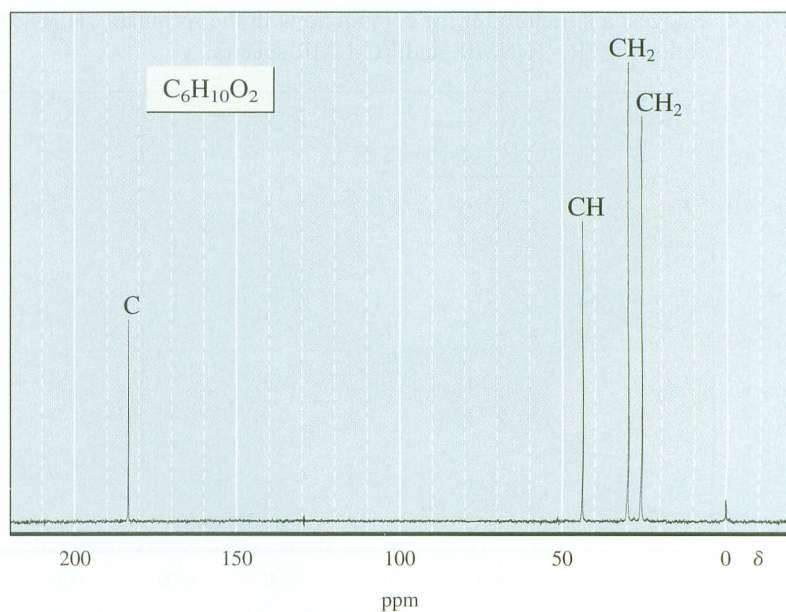




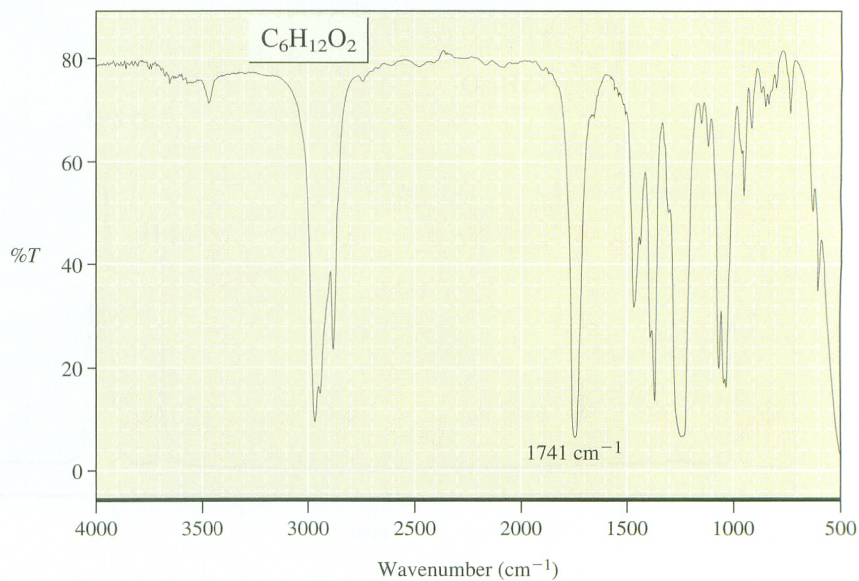
- 14.24** Suggest a structure for the compound with the formula  $C_6H_{10}O_2$  that has the following IR,  $^1H$ -NMR, and  $^{13}C$ -NMR spectra:



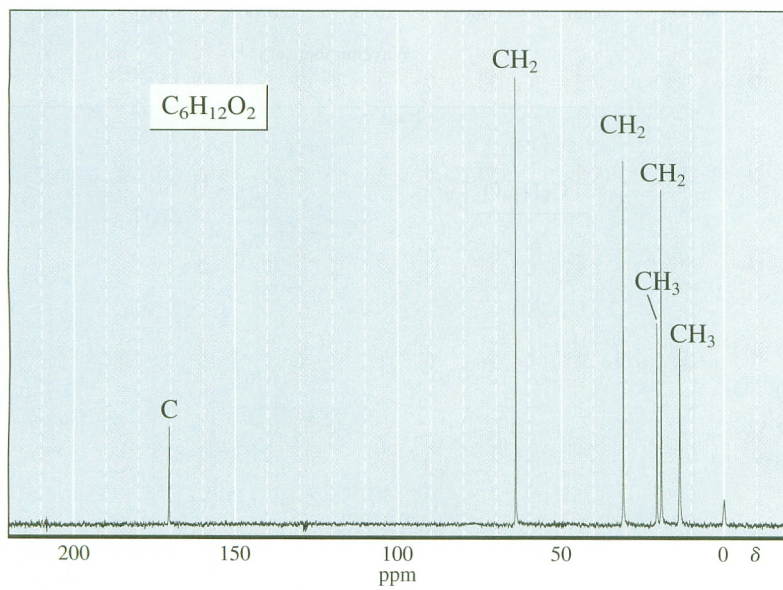
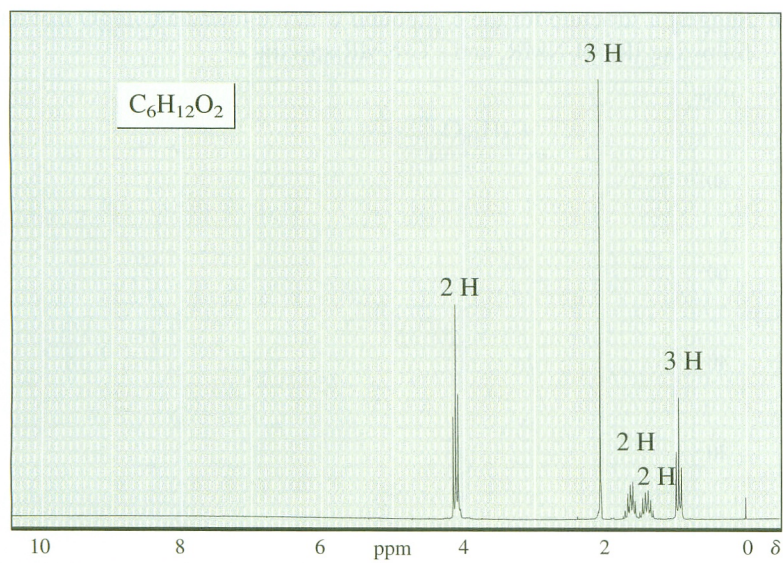




**14.25** Suggest a structure for the compound with the formula  $C_6H_{12}O_2$  that has the following IR,  $^1H$ -NMR, and  $^{13}C$ -NMR spectra:

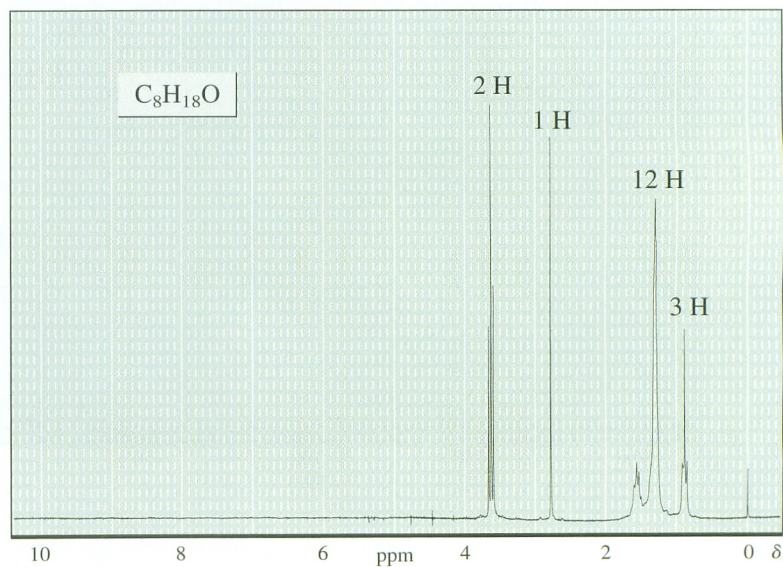
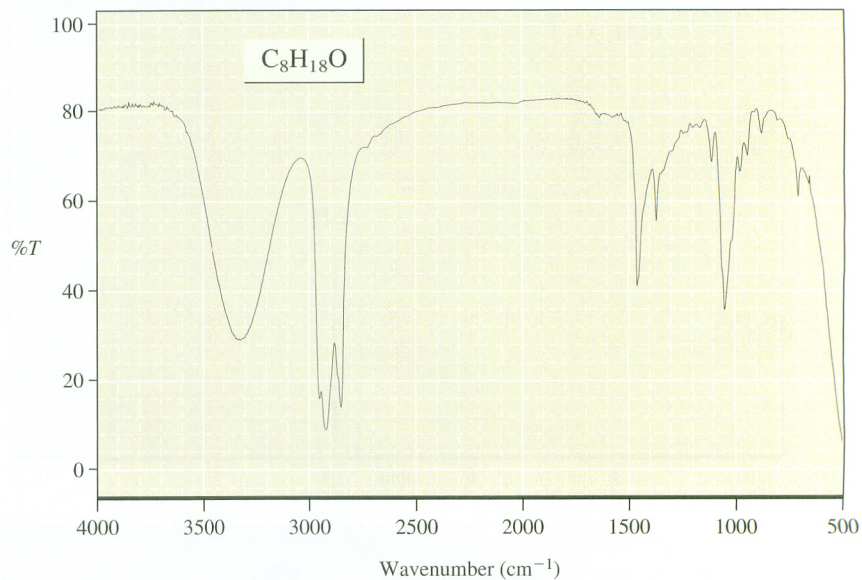




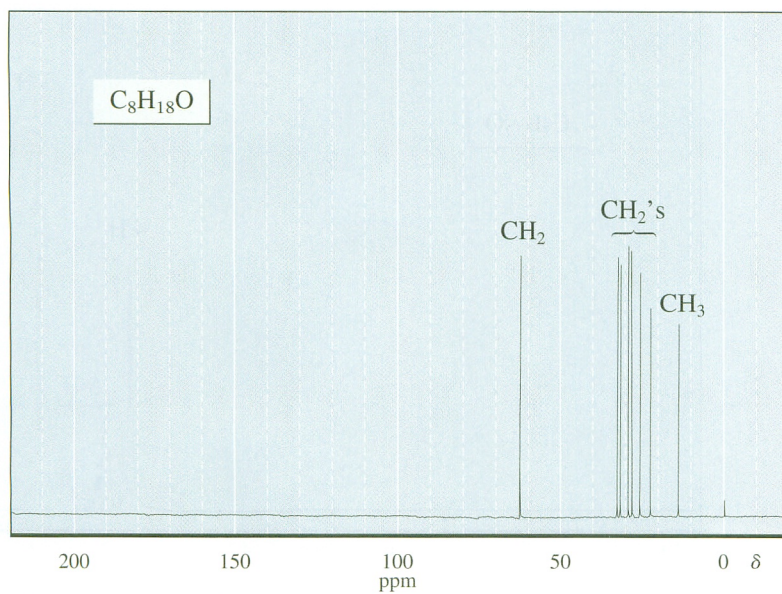




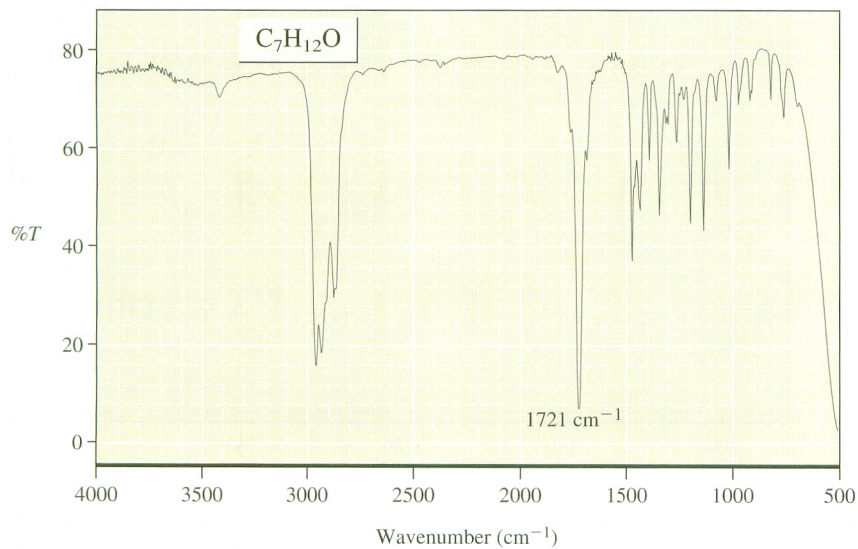
**14.26** Suggest a structure for the compound with the formula  $C_8H_{18}O$  that has the following IR,  $^1H$ -NMR, and  $^{13}C$ -NMR spectra:



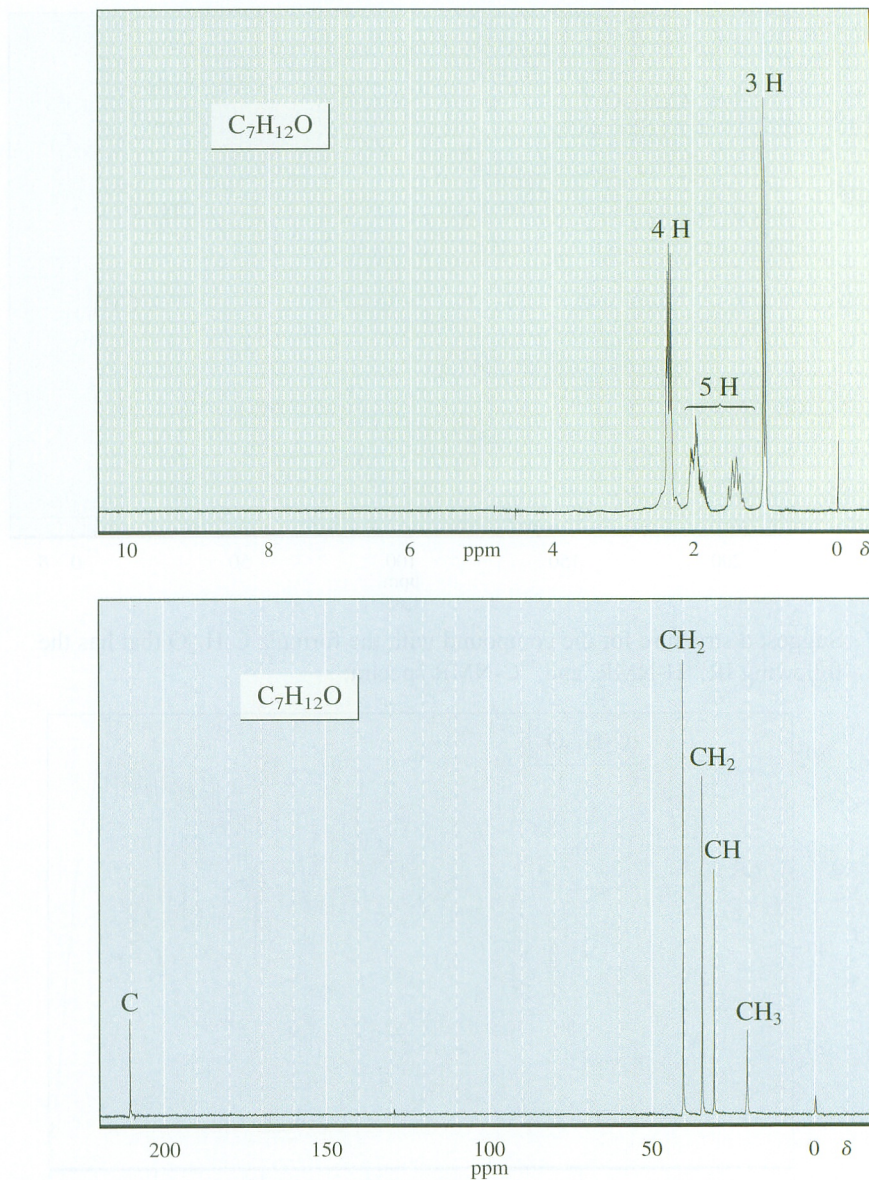




**14.27** Suggest a structure for the compound with the formula  $C_7H_{12}O$  that has the following IR,  $^1H$ -NMR, and  $^{13}C$ -NMR spectra:

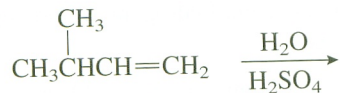




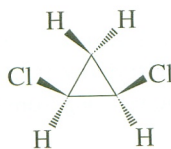


- 14.28** An unknown compound, **A** ( $C_7H_{10}$ ), shows four absorptions in its  $^{13}C$ -NMR spectrum, at 22 ( $CH_2$ ), 24 ( $CH_2$ ), 124 (CH), and 126 (CH)  $\delta$ . On reaction with excess  $H_2$  and a Pt catalyst, **A** produces **B** ( $C_7H_{14}$ ). **B** shows a single peak at 28.4  $\delta$  in its  $^{13}C$ -NMR spectrum. Ozonolysis of **A** gives  $C_2H_2O_2$  and  $C_5H_8O_2$ . Suggest structures for **A** and **B**.

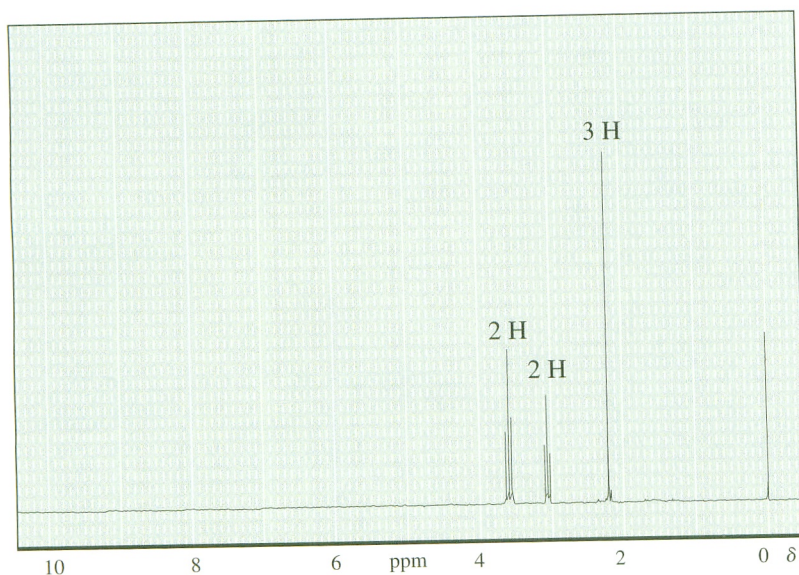
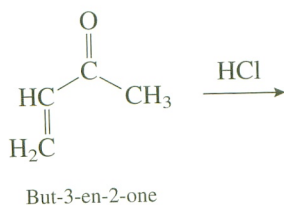
- 14.29** The product of the following reaction has a broad absorption at  $3330\text{ cm}^{-1}$  in its IR spectrum. Its  $^{13}\text{C}$ -NMR spectrum shows absorptions at 70 (C), 34 ( $\text{CH}_2$ ), 30 ( $\text{CH}_3$ ), and 15 ( $\text{CH}_3$ ). Suggest a structure for this compound.



- 14.30** Explain how many absorptions appear in the  $^1\text{H}$ -NMR spectrum of this compound:



- 14.31** The addition of  $\text{HCl}$  to but-3-en-2-one gives a product with the following  $^1\text{H}$ -NMR spectrum. Show the structure of this product, show a mechanism for its formation, and explain the regiochemistry of the reaction (see Section 11.2).





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## Problems Using Online Three-Dimensional Molecular Models

- 14.32** Explain how many different hydrogens would appear in the  $^1\text{H}$ -NMR spectra of these compounds.
- 14.33** Explain how many different signals would appear in the  $^{13}\text{C}$ -NMR spectra of these compounds.



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